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Reduced Smoke Propellant Binder Residue as a Fuel Source

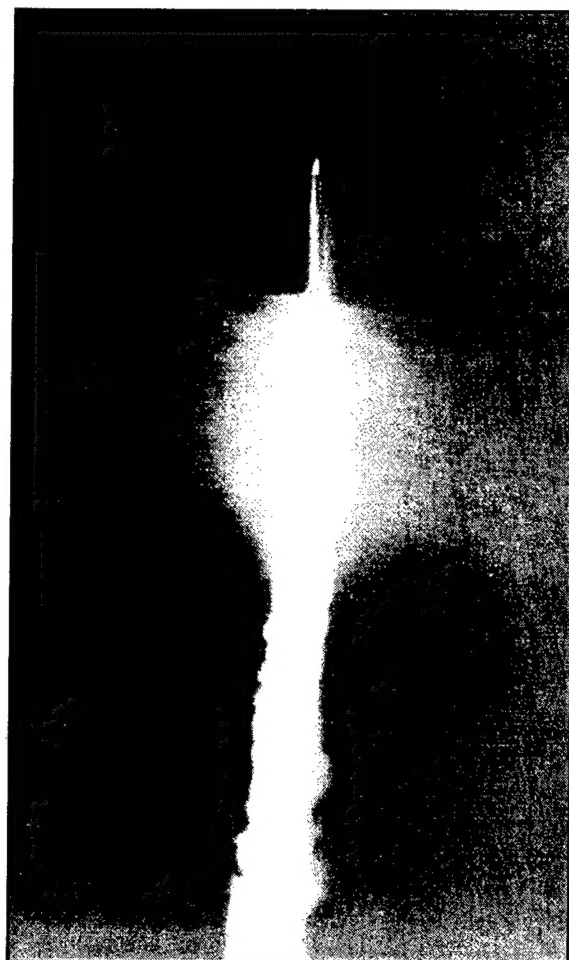
by

Kathryn F. Miks and Richard J. Scholze

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Preliminary data indicate that both the HARM and Maverick propellant binder residues are suitable for use as a low-grade fuel, and market research identified three combustion reuse options. All the applications require a very high volume of fuel at a low price. Combustion emissions may be an environmental concern depending on how the residue is integrated into the system. A related technical report (Miks and Scholze, TR 97/32) will refine and evaluate the alternate uses identified in this report.



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Foreword

This study was conducted for Headquarters, U.S. Army Corps of Engineers, under Project 4A162720D048, "Industrial Operations Pollution Control Technology"; Work Unit UP6, "Reduced Smoke Propellants." The technical monitor was Lou Kanaras, U.S. Army Environmental Center, SFIM-AEC-ETD.

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1 Introduction

Background

An estimated 8.8 million lb of reduced smoke propellant is targeted for demilitarization and disposal. Open burning/open detonation (OB/OD) areas have been used for disposal in the past but are being phased out as they become more stringently regulated. For example, the U.S. Army is in the process of closing over 50 percent of the available OB/OD sites at their installations. States are taking increasingly strong steps to minimize the impact on environmental air quality, even in isolated geographic regions. Recovery and beneficial reuse of propellant ingredients would reduce or minimize the quantity of waste requiring disposal. Recycling of ammonium perchlorate (AP), the primary propellant ingredient, has been established. Of the amount of propellant to be demilitarized, 1.5 million lb of binder residue is estimated to be reuseable. Reuse of the AP-depleted binder has been studied on a limited basis; however, only aluminized Class 1.3 propellants have been evaluated.

Objective

The objective of this study was to complete the first phase of a program to identify and evaluate alternate uses of Class 1.3 reduced smoke (nonaluminized) propellant binder residue, with a focus on use as a fuel or fuel supplement.

Approach

Researchers obtained 250 lb of binder residue reclaimed from approximately 1,000 lb of scrap HARM propellant processed through an AP reclamation facility. Residues were also obtained from Maverick and Sidewinder propellants processed through a pilot-scale reclamation apparatus. The residues were characterized via analytical, physical, and safety evaluations. Bench-scale combustion evaluations were performed to determine fuel values and to characterize the combustion products. One residue was burned in two pilot-scale facilities: a batch rotary kiln and a continuous spreader stoker. A survey of combustion processes was performed to determine reuse markets for binder residue.

Mode of Technology Transfer

Information from this research program will be transferred to the Army Environmental Center (AEC) to be used for demilitarization and propellant reuse programs.

Metric Conversion Factors

U.S. standard units of measure are used throughout this report. A table of metric conversion factors is presented below.

1 in.	=	25.4 mm
1 lb	=	0.453 kg
1 gal	=	3.78 L
°F	=	(°C × 1.8) + 32

2 Propellant Extraction and Characterization

Propellant Extraction

Three unique nonaluminized Class 1.3 propellant formulations were selected for binder residue evaluation. Table 1 lists the propellant types and ingredients.

HARM Propellant

Approximately 250 lb of binder residue were recovered from 950 lb of scrap HARM propellant (TP-H1159) processed through an AP reclamation facility. The propellant exhibited good cutting characteristics, although it was described as "stickier" than traditional aluminized formulations, causing minor filter plugging.

Maverick Propellant

The Maverick propellant (TP-H8254) was not processed through the pilot facility because insufficient material could be obtained in time to support program schedule requirements. Instead, AP was extracted from 9.3 lb of Maverick propellant using a 5-gal pilot-scale apparatus. Cured propellant samples were cut into 1/16-in.-thick slices and extracted with 160 °F water for 2 hr. Approximately 9 lb of wet residue were recovered. AP and moisture analyses showed the material to contain 27 percent AP (dry content) and 32 percent moisture. Because of the high AP content, the residue was extracted for an additional 6.5 hr with fresh water. Approximately 11.9 lb of wet residue were recovered.

Table 1. Class 1.3 propellant types and ingredients.

HARM TP-H1159	Maverick TP-H8254	Sidewinder TP-H8288
R-45M polymer IPDI AP HX-752 Carbon black Al ₂ O ₃ Oxamide	R-45M polymer IPDI AP HX-752 Graphite Al ₂ O ₃ DOA ZrC FeF ₃ Flexone DTBH	R-45M polymer DDI AP HX-752 RDX DOA ZrC Flexone DTBH
R-45M polymer = polybutadiene, hydroxyl-terminated IPDI = isophorone diisocyanate AP = ammonium perchlorate HX-752 = propylene imine adduct of isophthalic acid Oxamide = H ₂ NOC(=O)CONH ₂ DOA = dioctyl adipate Flexone = n-cyclohexyl-n'-phenyl-p-phenylenediamine DTBH = di(tert-butyl)hydroquinone DDI = dimethyl diisocyanate RDX = cyclotrimethylenetrinitramine		

ered from the second extraction. The residue was dewatered in the reclamation facility basket centrifuge.

Sidewinder Propellant

The Sidewinder propellant (TP-H8288) was not processed through the pilot facility because processing cyclotrimethylenetrinitramine (RDX) would have required costly safety evaluations and facility cleanup. Rather, the material was processed through the 5-gal pilot apparatus so that the process and binder residue could be evaluated on a safer and more cost effective scale.

Before processing the Sidewinder propellant on the pilot scale, a laboratory-scale extraction was performed and standard safety tests were run to ensure that the process could be safely scaled up. AP was extracted from approximately 300 g of Sidewinder propellant. Cured propellant samples were sliced into 1/16-in.-thick pieces and extracted with 160 °F water for 26 hr. The residue was dewatered in the reclamation facility basket centrifuge. Safety analyses results indicated that the material would be acceptable to scale up to the 5-gal batch size.

After the safety tests, AP was extracted from 9.7 lb of Sidewinder propellant using the 5-gal pilot-scale apparatus. Cured propellant samples were prepared by slicing into 1/16-in.-thick pieces which were extracted with 160 °F water for 2 hr. Approximately 10.1 lb of wet residue were recovered. The residue was extracted with fresh water for an additional 5 hr (total time = 7 hr), after which approximately 9.8 lb of wet residue were recovered. The residue was dewatered in the reclamation facility basket centrifuge.

Binder Residue Characterization

The residues were characterized by chemical, safety, and mechanical property evaluations. The following chemical analyses were performed: percent moisture, percent AP, carbon-hydrogen-nitrogen (CHN) elemental analyses, RDX content (Sidewinder only), and trace metals. Table 2 gives the results of the analyses.

Chemical Properties

Moisture content. Moisture was determined via loss-in-weight gravimetric analyses at 105 °C. All values were higher than the nominal 20 to 30 percent observed with traditional aluminized propellants (HARM, 37 percent; Maverick, 62 percent; and Sidewinder, 62 percent).

Table 2. Propellant binder residue composition.

	HARM Residue	Maverick Residue	Sidewinder Residue
Moisture, %	37	62	62
AP, %	6.6	34.9	6.2
RDX, %	--	--	21.6
Elemental analysis, %			
Carbon	72.98	50.13	64.70
Hydrogen	8.50	8.96	15.08
Nitrogen	8.57	4.77	7.45
Oxygen	6.42	20.39	6.14
Chlorine	2.00	10.53	1.10
Aluminum oxide	1.10*	2.17*	--
Zirconium carbide	--	2.17*	5.21*
Trace metals	<u>0.43</u>	<u>0.88</u>	<u>0.32</u>
	100.00	100.00	100.00
Trace metals, ppm			
Aluminum	--	--	134
Calcium	2794	1716	2206
Iron	169	6212	84
Magnesium	72	49	32
Manganese	ND	31	ND
Molybdenum	ND	29	ND
Phosphorous	1216	442*	568*
Silver	ND	22	42
Sodium	44	237	173
Strontium	<u>ND</u>	<u>13</u>	<u>27</u>
	4295	8751	3266
All values (except Moisture) are reported based on dried content. All values were determined from triplicate samples.			
*Values based on theoretical predictions			

AP content. Ammonium perchlorate was determined with ion chromatography (IC-perchlorate) of methanol Soxhlet extractions dried and dissolved in deionized water. The HARM and Sidewinder residues contained approximately 6 percent AP, which is typical of aluminized propellant residues. For the Maverick residue, both moisture and AP levels increased after the second extraction (from 32 percent moisture/27 percent AP to 62 percent moisture/35 percent AP). It appears that this material picked up AP-concentrated water in the basket centrifuge; Maverick residue has a particularly spongy characteristic that likely created a nonhomogeneous material. These results, therefore, are only qualitatively reliable.

Elemental analysis. CHN elemental analyses were performed by combusting the material with O₂ at 1,742 °F and measuring the gaseous combustion products with a thermal conductivity detector.

Trace metal analysis. Trace metals were determined from inductively coupled plasma (ICP) analyses of acid-digested samples. Although ICP does not test for aluminum oxide or zirconium carbide (they are insoluble in the digestion), these materials are expected to be present at the levels indicated, based on the initial propellant formulations. Calcium and phosphorous were observed in all of the residues. These metals are present in AP as tricalcium phosphate (used as an anti-caking agent). An appreciable level of iron was observed in the Maverick residue due to ferric fluoride in the propellant. Other metals were observed at trace levels and are likely present as such in either the raw materials or process water. No unusual constituents were observed. For the Sidewinder residue, RDX was determined with high performance liquid chromatography (HPLC) followed by solvent leaching with acetonitrile. The 22 percent RDX measured agrees well with the theoretically predicted 24 percent.

The observed constituents and concentrations correlate well with the theoretically predicted levels.

DSC and TGA analysis. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were completed on all of the propellant residues. DSC measures exothermic and endothermic decomposition or phase transition events that occur as the sample is heated. TGA measures weight changes due to evaporation, pyrolysis, combustion, etc. that occur as the sample is heated.

DSC analysis. Before testing, the DSC samples were dried. A Perkin-Elmer DSC-4 differential scanning calorimeter was used to analyze the residues. Samples were heated at a rate of 20 °C/min over a temperature range of 30 to 400 °C. Before testing, small samples (about 2 mg) were placed into hermetic cold-weld sealed aluminum capsules with a 15-microliter internal volume.

Figures 1 through 7* show the DSC results. Figure 7 shows an empty pan DSC baseline. For the HARM residue (Figures 1 and 2), an exotherm starts in the vicinity of 240 °C. The energy associated with the exotherm is difficult to quantify because of sharp endothermic spikes in the scans, which are probably due to pan leaks (which, in turn, suggests that the drying procedure may not have removed all of the water). The presence of this exotherm does not necessarily indicate that the material is "live," as many inert plastics and elastomers show exotherms with associated energies of hundreds of calories per gram when heated in hermetic DSC capsules. The origin of such exotherms is probably endothermic pyrolysis of the material to yield low molecular weight gaseous species followed by exothermic

* Figures are shown at the end of the chapter.

crosslinking of the unsaturated residue left behind. Also, neither scan shows the characteristic AP crystal phase transition endotherm at 240 °C, which suggests that little or no crystalline AP is in the samples.

For the Sidewinder residue (Figures 3 and 4) an exotherm starts at about 190 °C. The energy associated with decomposition is at least 650 cal/g for the sample in Figure 3 and at least 318 cal/g for the sample in Figure 4. The scan in Figure 3 shows an endothermic peak at about 240 °C superimposed on the exotherm, which may be indicative of an AP crystal phase transition. With both scans (Figures 3 and 4), the exotherm becomes quite sharp at 240 °C, which may be indicative of live material.

The Maverick residue (Figures 5 and 6) also shows an exotherm starting at about 220 °C and becoming fairly sharp above 240 °C. As shown in the next section, this exotherm correlates with a sharp mass loss in TGA, suggesting the presence of live material. A small AP phase change endotherm at about 240 °C, with a transition energy similar to that of the Sidewinder residue sample, was also observed.

TGA analysis. TGA samples were tested in the as-received state, with no additional sample preparation. Samples were tested on a Perkin-Elmer TGS-2 thermogravimetric analyzer in a flowing air atmosphere at a heating rate of 20 °C/min over a temperature range of 40 to 900 °C. Sample sizes were on the order of 3 to 10 mg.

Figures 8 through 14 show TGA scans. For the HARM residue (Figures 8 and 9), a mass loss occurred between 40 and 160 °C, which suggests the substantial presence of volatile material (probably water). The apparent moisture content is about 35 to 40 percent, which agrees very well with the earlier measurements of 37 percent. The ash content (material left over after burning) appears to be on the order of 2.5 to 3 percent. Several other mass losses above 160 °C probably represent pyrolysis or combustion steps.

TGA results for the Sidewinder residue are shown in Figures 10 through 12. A significant amount of apparent moisture was present, approximately 50 to 60 percent, which also agrees very well with the earlier measurements of 62 percent. The ash content is on the order of 3 percent. In one of the runs (Figure 10), a sharp mass loss occurs at the same temperature as in the DSC scan of Figure 4 (about 240 °C). This loss, together with the DSC scan, suggests the presence of live material.

TGA results for the Maverick residue are shown in Figures 13 and 14. The material had a 45 to 55 percent moisture content as measured by TGA, slightly lower than

to explosion or detonation, Russian deflagration-to-detonation tests (DDTs) were performed on the wet material. All test results were negative ("no go"), indicating that no explosion potential exists with burning wet residue. Additional testing is recommended to evaluate the dried material. Furthermore, it is recommended that the Russian detonation susceptibility test (DST) be performed on both wet and dry residues to evaluate potential mass detonation hazards, and that unconfined burn tests be performed on the Maverick and Sidewinder residues to evaluate potential mass fire hazards (these residues had high AP and RDX percentages, respectively).

Mechanical Properties

Mechanical tests were conducted on the HARM and Maverick residues to determine if the material would adhere to common materials and to characterize its mechanical properties. The results were evaluated by Braithwaite (1994). Rheometrics Dynamic Spectroscopy (RDS), uniaxial tensile, and tensile adhesion tests were run on the residues, which were shown to be high elongation, low strength, viscous solids. The low strength and stiffness would make it extremely difficult to form any sort of self-supporting structure from the materials. Temperature changes were shown to have little effect on the stiffness of the residue over the range of 50 to 180 °F. Torsional stiffness increased moderately with strain rate. The material tended not to adhere to common surfaces (steel, aluminum, Teflon™, and glass) even after drying (i.e., the cohesive strengths of the material were higher than their adhesive strengths). Because the Sidewinder residue was so similar in nature to the other residues, and to conserve resources, mechanical tests were not conducted on the Sidewinder residue.

RDS tests. After placing a residue sample between two parallel metal plates, one of the plates is then twisted back and forth, placing the material in shear. The RDS machine automatically measures the torque and reports the results in terms of storage and loss modulus. Two different types of RDS tests were run: (1) an ambient temperature frequency sweep to determine rate sensitivity and (2) a constant frequency (1 Hz) temperature sweep to determine temperature sensitivity. All of the tests were run at a strain amplitude of 3 percent.

The results of the RDS temperature sweep are shown in Figures 15 and 16. Both materials show almost no temperature dependence over the tested range of 50 to 180 °F. Figures 17 and 18 show the results of the RDS frequency sweep. The residues show a moderate stiffness increase with increasing strain rate. The rate sensitivity is less than that of typical Class 1.3 cured propellants.

In Figures 15 through 18, G' represents the materials storage shear modulus, a measure of the energy transferred elastically through the specimen, while G'' represents the flow modulus, a measure of the energy lost to viscous dissipation. Tan Delta represents the ratio G''/G' . For example, a metal would have a high storage modulus and low loss modulus (Tan Delta ~ 0), while a low viscosity liquid would have a low storage modulus and high loss modulus (Tan Delta > 1). Storage modulus for both residues is several orders of magnitude lower than the storage modulus for a typical cured Class 1.3 propellant.

To form the tensile samples, the material was pressed flat and die-cut into a half-sized JANNAF* dog bone configuration. The specimens were highly irregular in geometry, since the material would not flow to form a flat sheet. The tests were conducted at a displacement rate of 2 in./min at ambient temperature.

Tensile tests. Table 4 shows tensile test results. However, the results shown may be somewhat misleading because of the irregular shape and/or composition of the samples. The material tended to stretch and break at one localized spot on the sample. The spot that strained was either thinner than the rest of the gauge section or had a higher-than-usual moisture content. Due to this localized straining, the actual stress and strain capability is probably understated in the Table. As proof of this, the adhesion tests show cohesive strength that exceeds the maximum stress obtained in the tensile tests.

Table 4. Propellant binder residue tensile test results.

Residue Type	Sample No.	Area	$E^{1.3}$ (psi)	ϵ_1 (%)	σ_m (psi)
HARM	1	0.658	2.6	129	3.0
	2	0.436	3.9	110	3.7
	3	0.579	4.4	91	3.1
	Average		3.7	110	3.3
	Std Dev		0.9	19	0.5
	CV (%)		25.4	17.2	14.1
Maverick	1	0.0628	23	104	8.4
	2	0.0652	17	76	8.5
	3	0.0706	16	106	11.8
	4	0.0684	16	140	14.2
	Average		18	106	10.7
	Std Dev		3.4	26	2.8
	CV (%)		18.8	24.8	26.4

* Joint Army, Navy, NASA, Air Force Interagency Propulsion Committee.

Because of the lack of uniformity in the samples, the uniaxial tensile results are of little quantitative value. Qualitatively, the results show the material to be very low strength and stiffness, with a high elongation capability, as compared with the properties of cured propellant.

Adhesion samples were formed by pressing the material between two adherends. The adherend materials were D6AC steel, 7075 aluminum, glass (Lexan™), and Teflon™. Since the high moisture content of the material could lead to poor adhesion, some of the samples were dried overnight at elevated temperatures. The HARM residue samples were dried at 100 °F and 135 °F and were tested before the Maverick residue samples. Because the HARM residue results showed no difference in properties with drying temperature, only one drying temperature (135 °F) was used for the Maverick residue tests. All tests were conducted after the samples had been allowed to cool to ambient temperature at a rate of 2 in./min. The nominal thickness of the residue between the adherends was 0.1 in.

Table 5 lists the maximum loads and corresponding nominal stresses for each of the samples. The results show that drying the samples increased the adhesion strength but not enough to exceed the cohesive strength of the material. The failure mode for all the tests was adhesive at the residue-to-adherend interface. The drying temperature did not appear to have any effect on the bond strength. Note that the samples listed as having a 75 °F drying temperature contained a great deal of moisture; these samples show less bond strength than the "dry" specimens. Surprisingly, after drying the HARM residue, the adhesion to the Teflon™ surface was as strong as the adhesion to the other surfaces. Before drying, the residue would not stick to the Teflon™ with enough strength to support the weight of the adherend. The dried Maverick residue, however, would not stick to a Teflon™ surface with enough adhesion strength to allow a test to be conducted.

The results of these analyses show that adhesion of the residue to any processing equipment should not be a concern.

Table 5. Tensile adhesion test results.

Residue Type	Sample No.	Adherend Material	Drying Temperature (°F)	σ Max (psi)
HARM	26	Glass	75	1.740
	27	Glass	75	0.303
	28	Glass	75	0.353
	5	Aluminum	75	1.250
	4	Steel	75	2.820
	6	Teflon™	75	~ 0
	7	Glass	100	5.100

Residue Type	Sample No.	Adherend Material	Drying Temperature (°F)	σ Max (psi)
HARM	8	Glass	100	8.820
	9	Glass	100	7.700
	10	Aluminum	100	15.300
	11	Aluminum	100	8.670
	12	Teflon™	100	7.620
	13	Teflon™	100	13.000
	14	Steel	100	11.800
	15	Steel	100	14.200
	16	Steel	100	11.500
	17	Glass	135	8.370
	18	Glass	135	6.470
	19	Glass	135	12.600
	20	Aluminum	135	6.250
	21	Aluminum	135	10.900
	22	Aluminum	135	3.680
	23	Steel	135	13.400
	24	Steel	135	6.510
	25	Steel	135	5.170
Maverick	5	Glass	135	4.9
	6	Glass	135	1.5
	7	Glass	135	9.3
	8	Glass	75	1.1
	9	Glass	75	0.6
	10	Glass	75	0.8
	11	Teflon™	135	~0
	12	Teflon™	135	~0
	13	Teflon™	135	0.3
	14	Steel	135	12.2
	15	Steel	135	12.7
	16	Steel	135	11.7
	17	Aluminum	75	1.1
	18	Aluminum	75	1.3
	19	Aluminum	135	15.7
	20	Aluminum	135	16.2
	21	Aluminum	135	16.7
	22	Teflon™	135	~0
	23	Teflon™	135	~0
	24	Teflon™	135	~0
Note: Failure mode for all samples was adhesive at the adherend interface.				

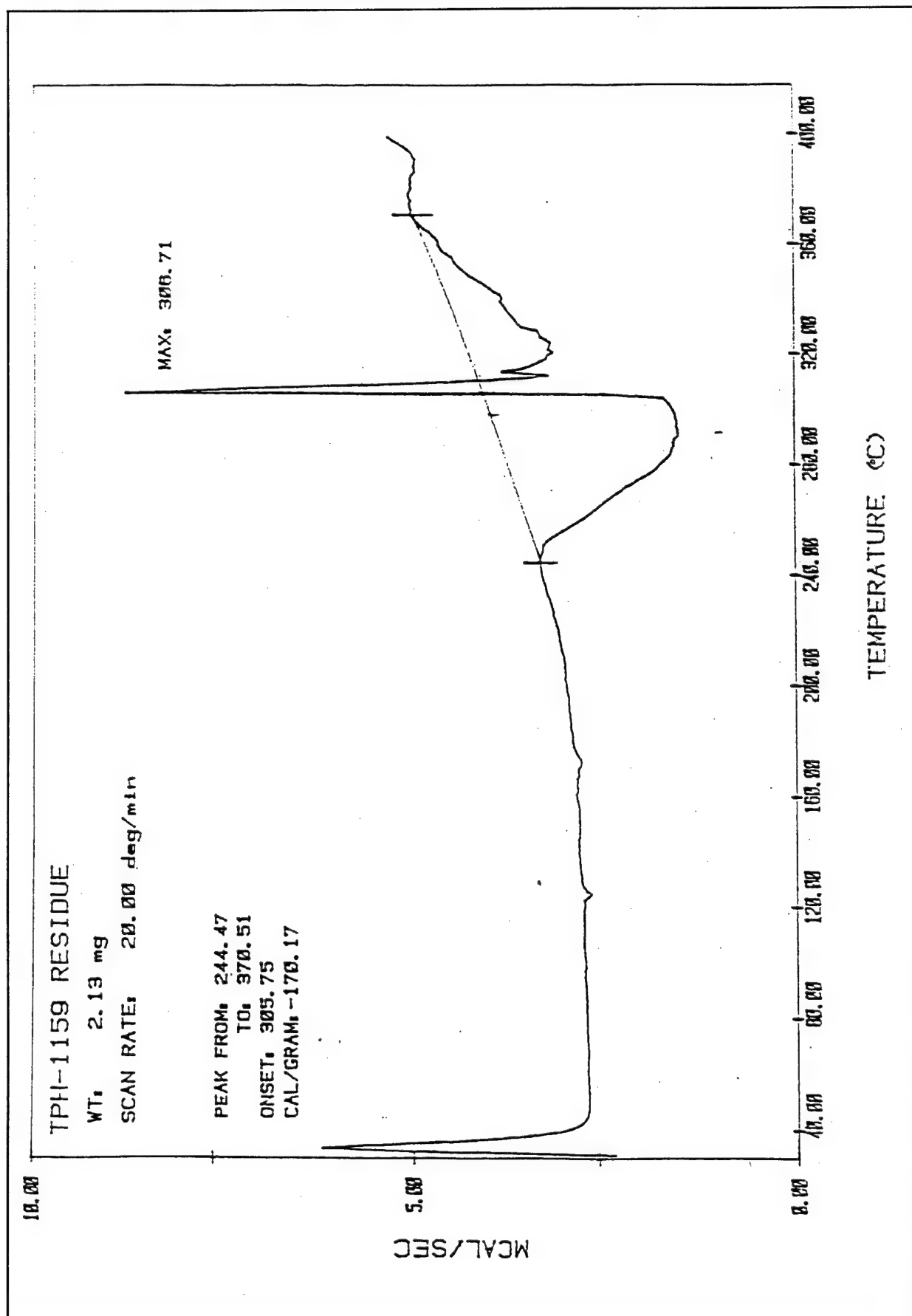


Figure 1. HARM residue DSC trace, Test 1.

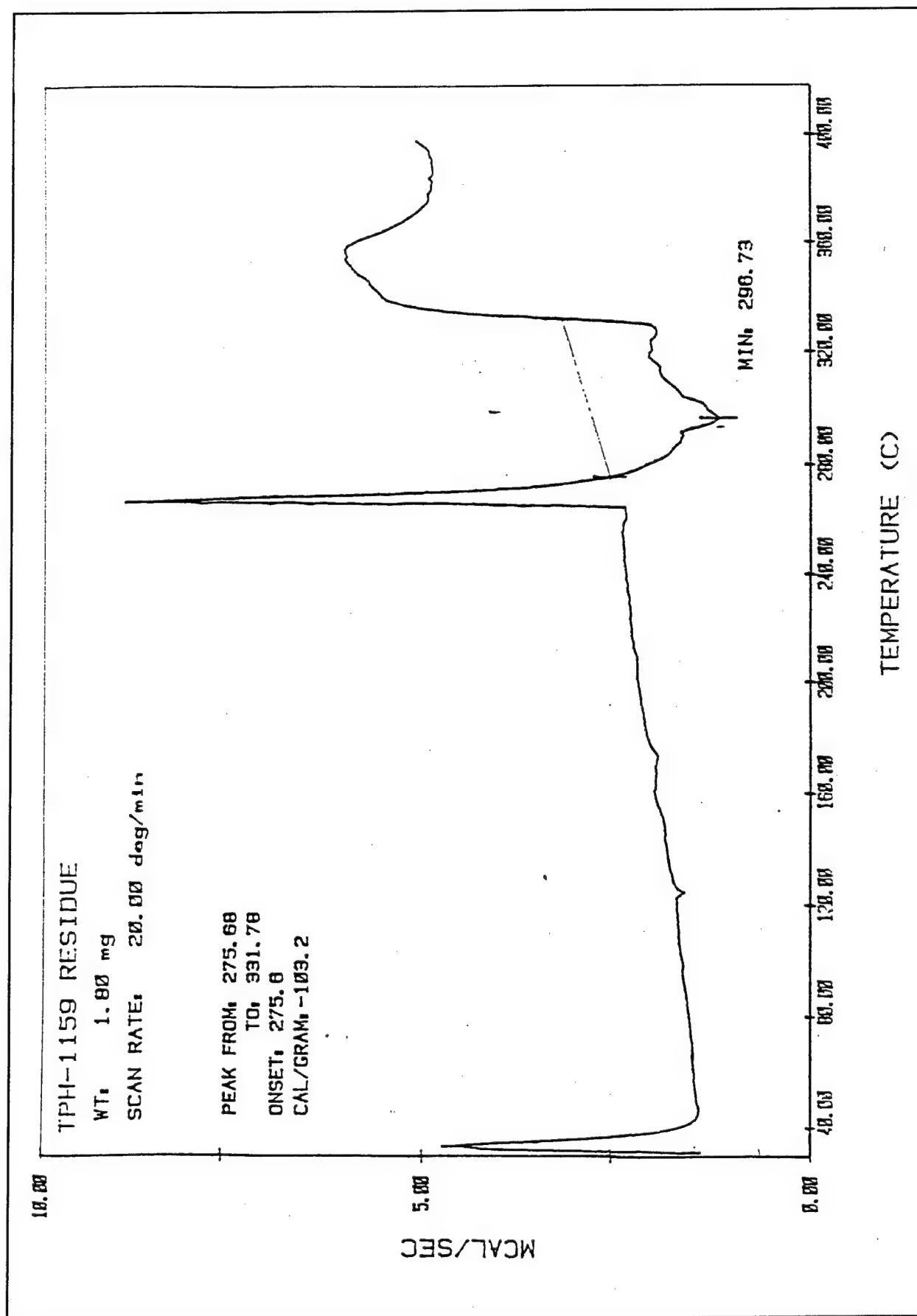


Figure 2. HARM residue DSC trace, Test 2.

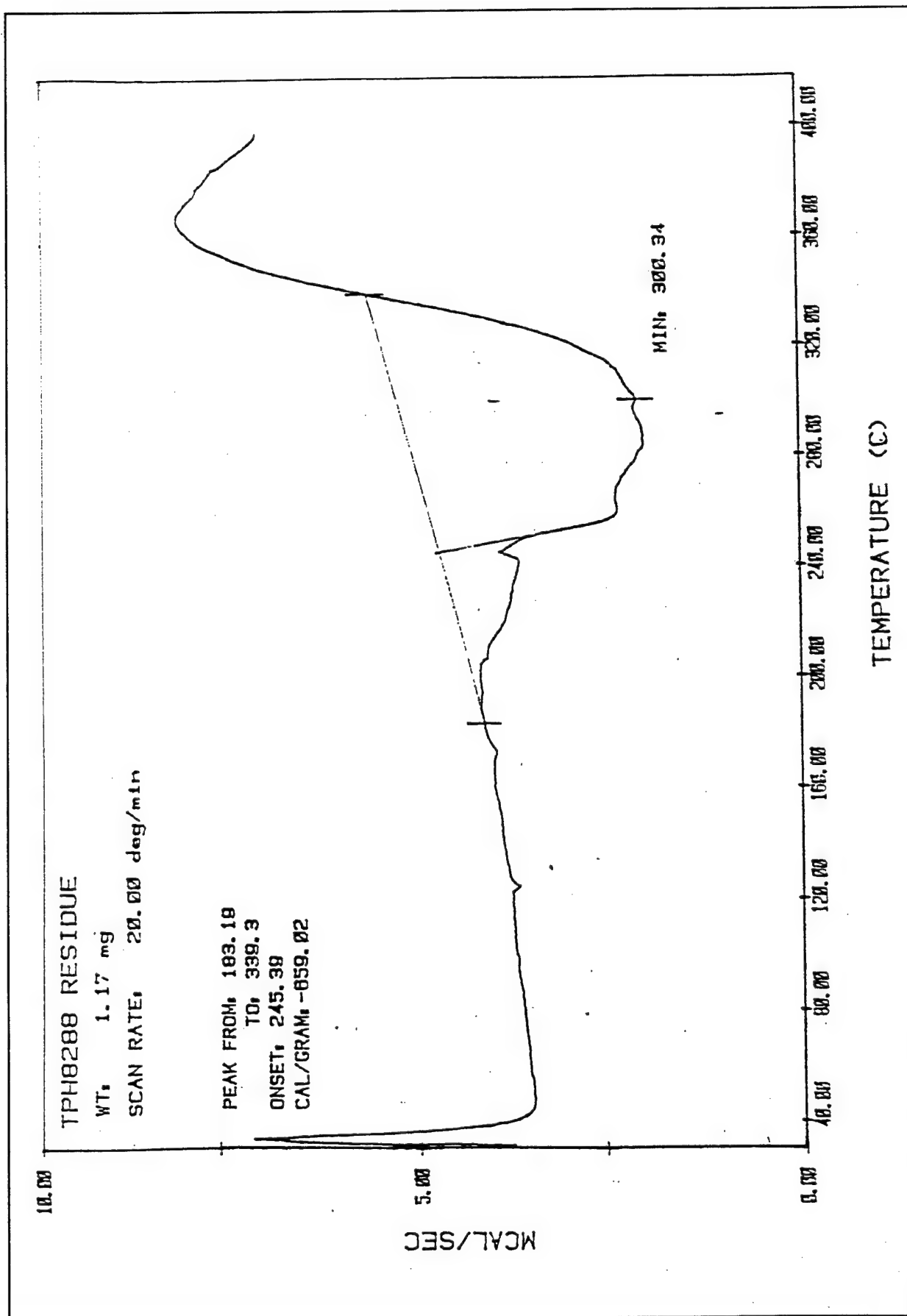


Figure 3. Sidewinder residue DSC trace, Test 1.

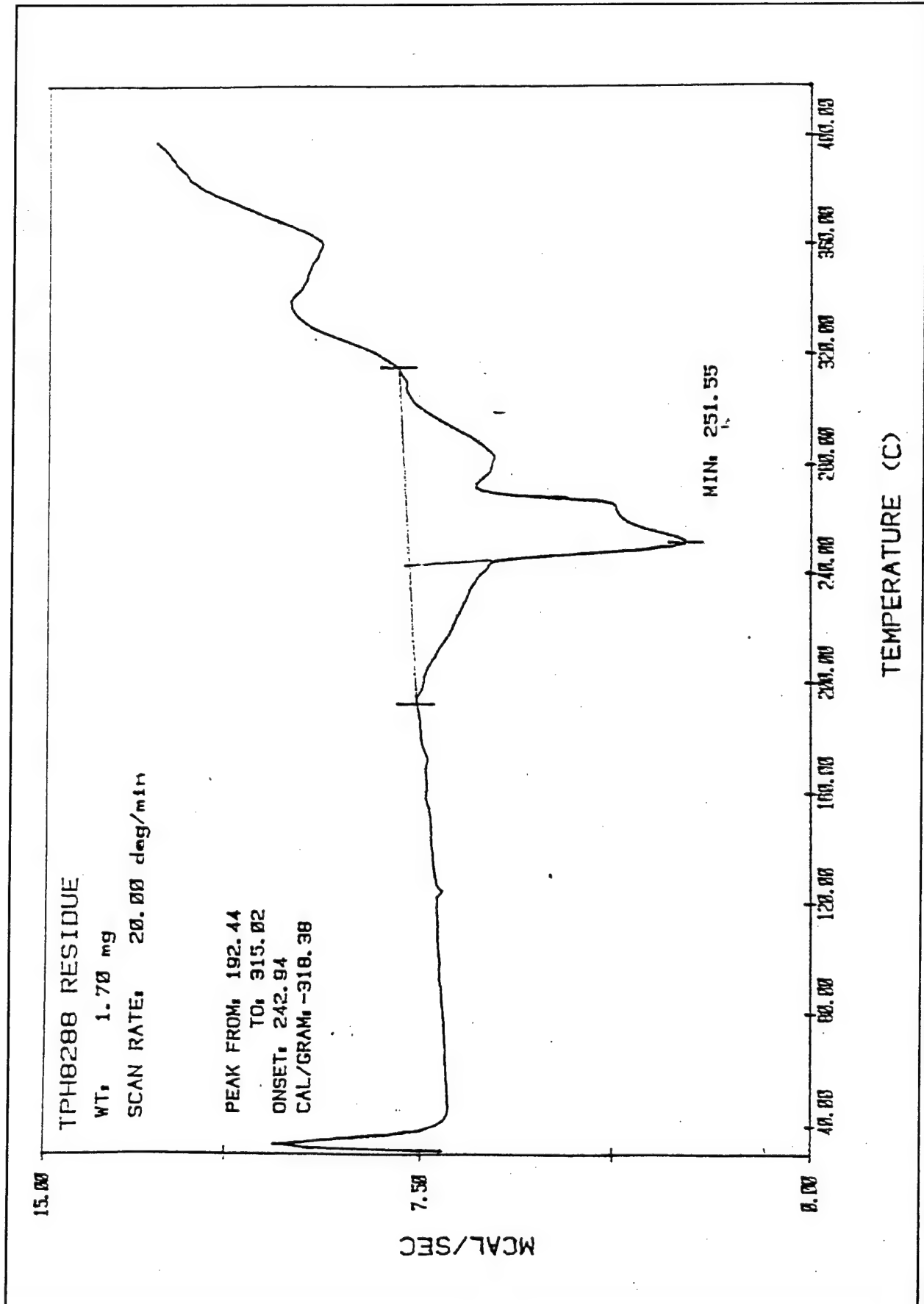


Figure 4. Sidewinder residue DSC trace, Test 2.

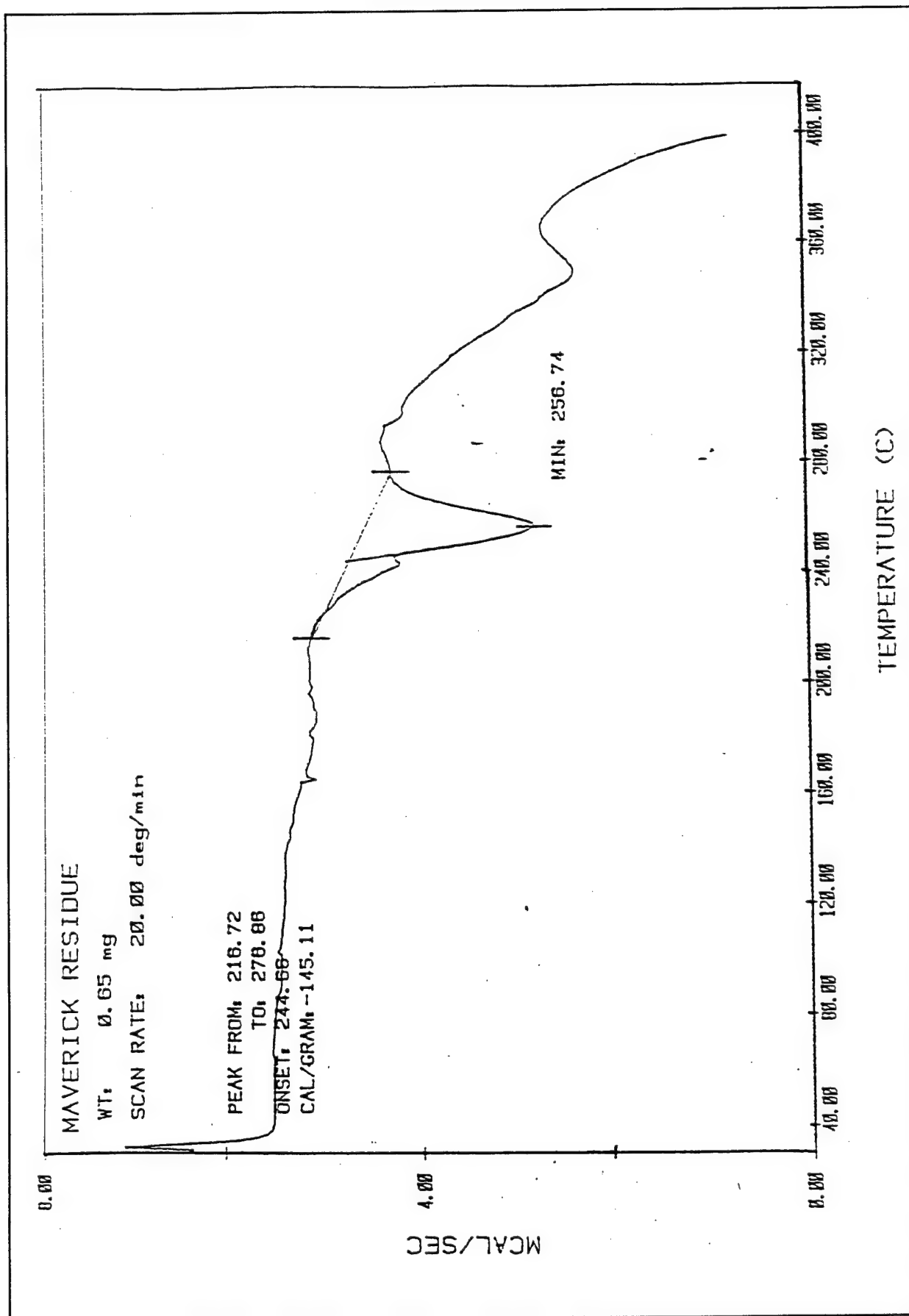


Figure 5. Maverick residue DSC trace, Test 1.

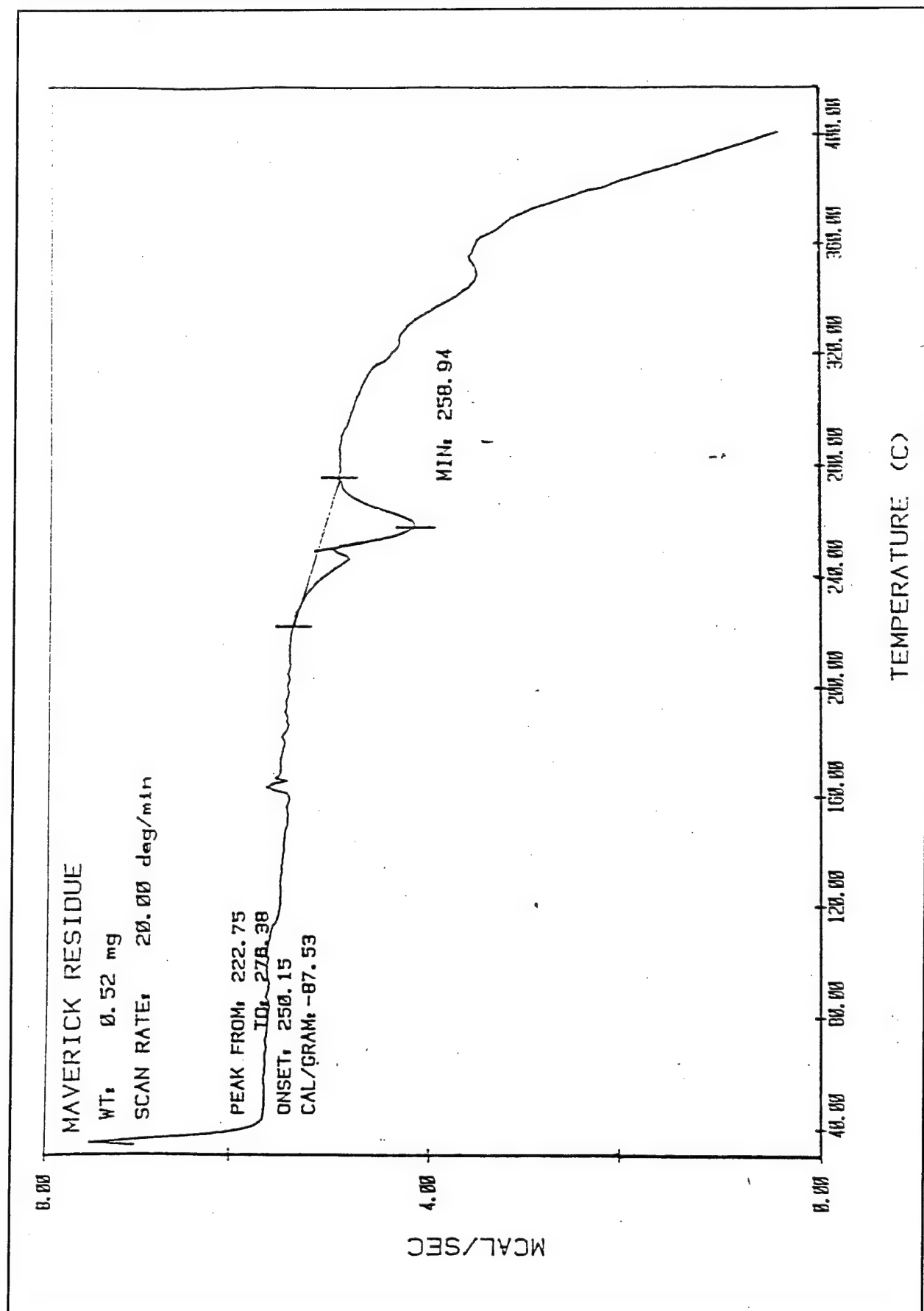


Figure 6. Maverick residue DSC trace, Test 2.

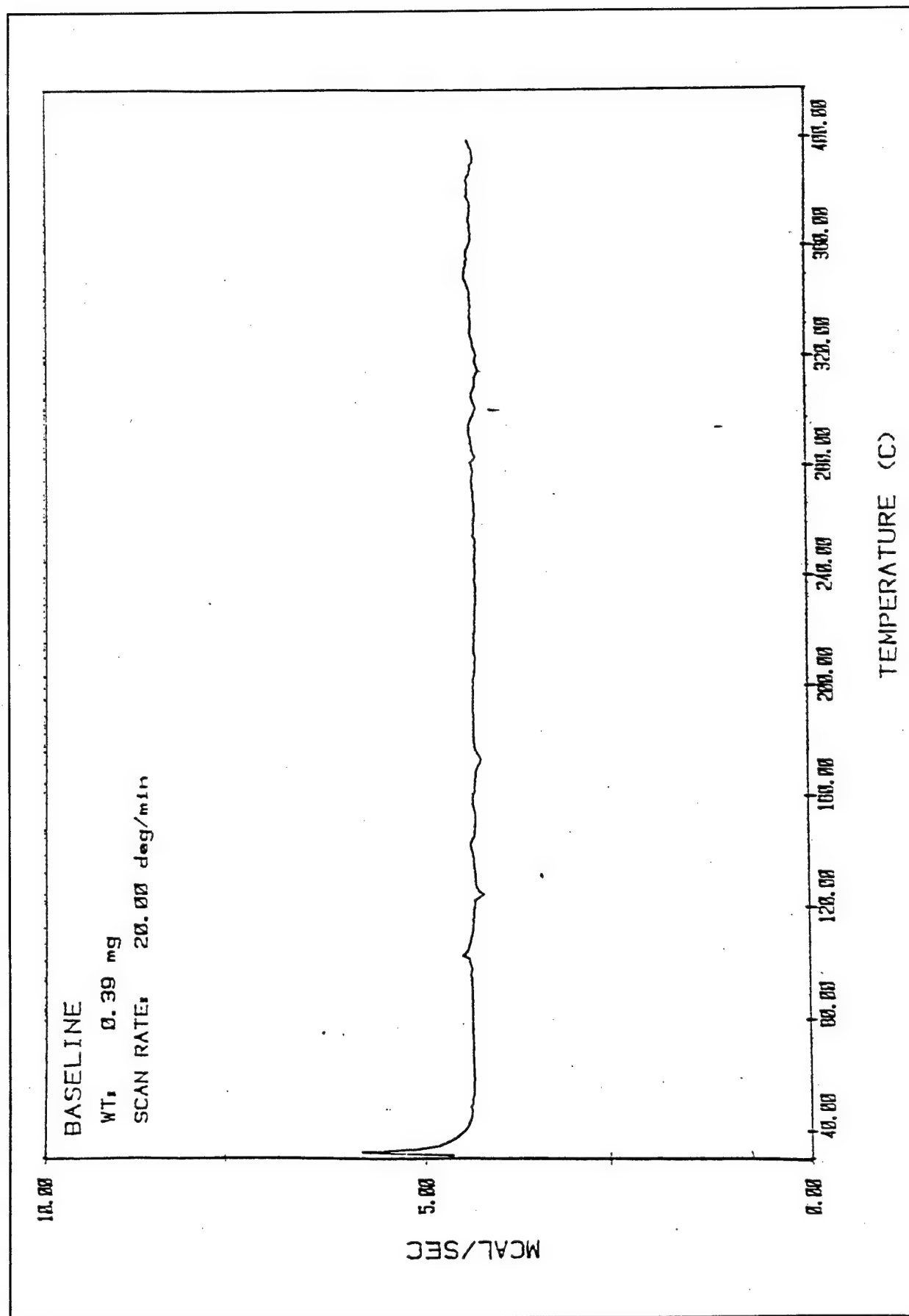


Figure 7. DSC baseline trace.

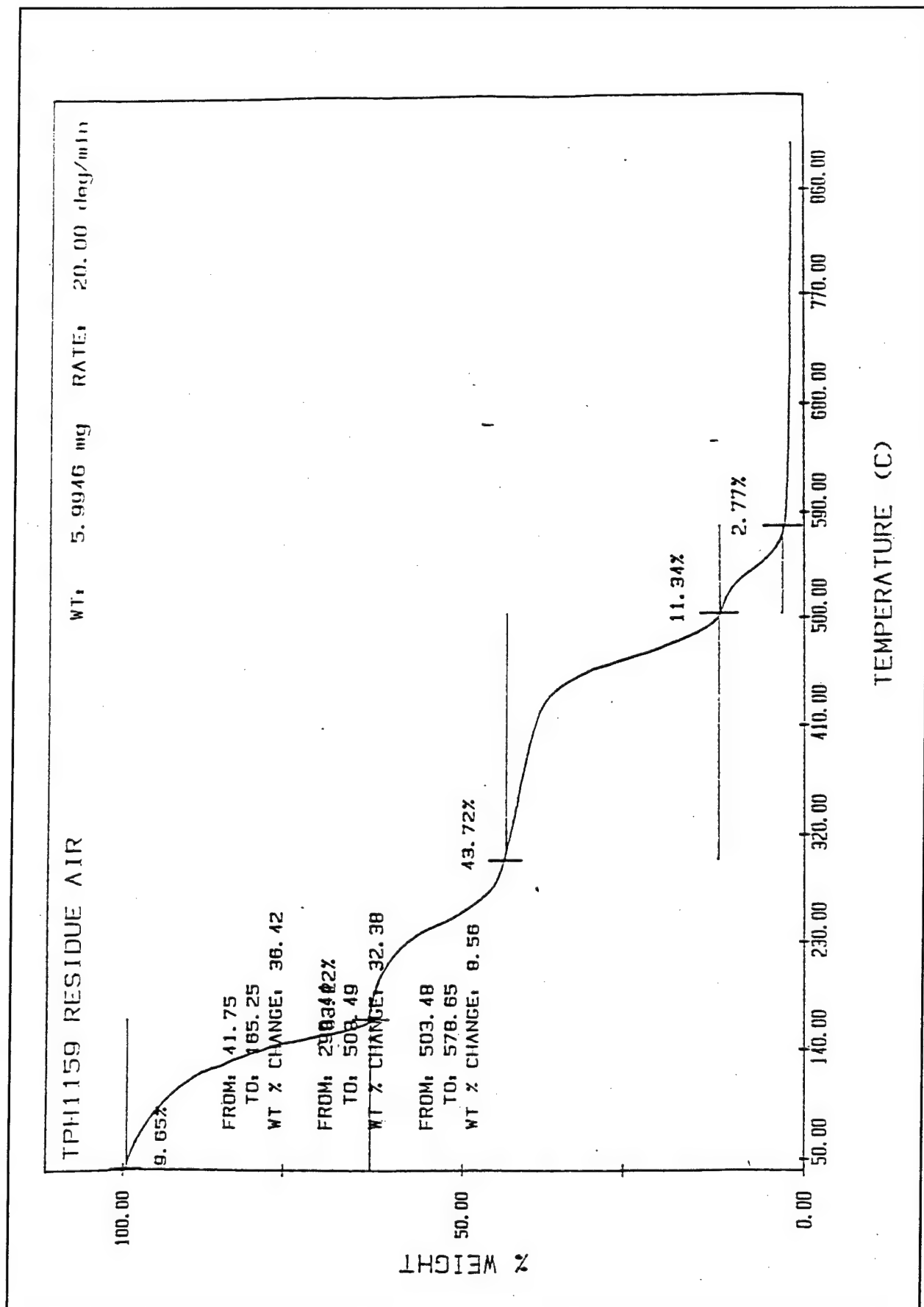


Figure 8. HARM residue TGA trace, Test 1.

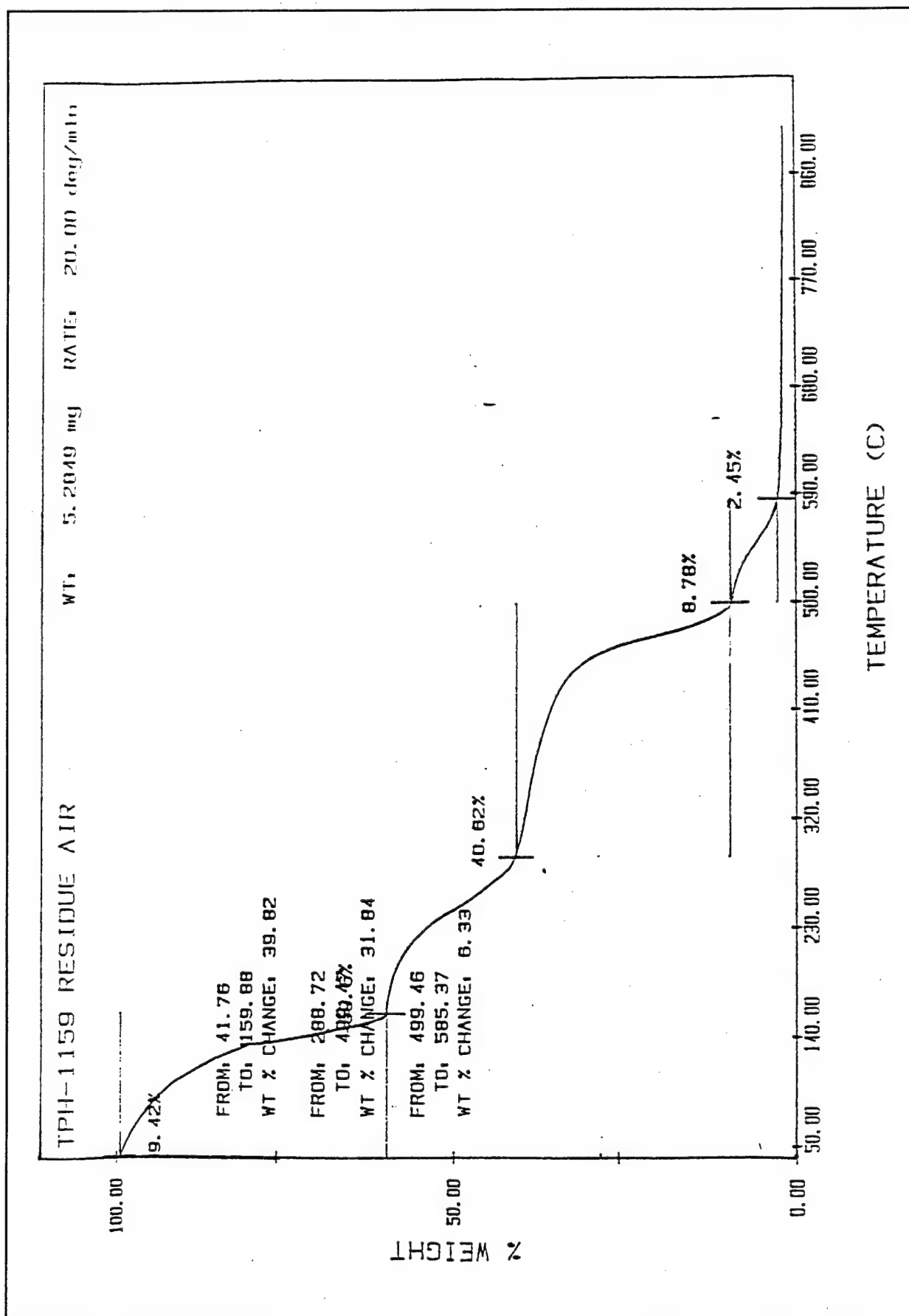


Figure 9. HARM residue TGA trace, Test 2.

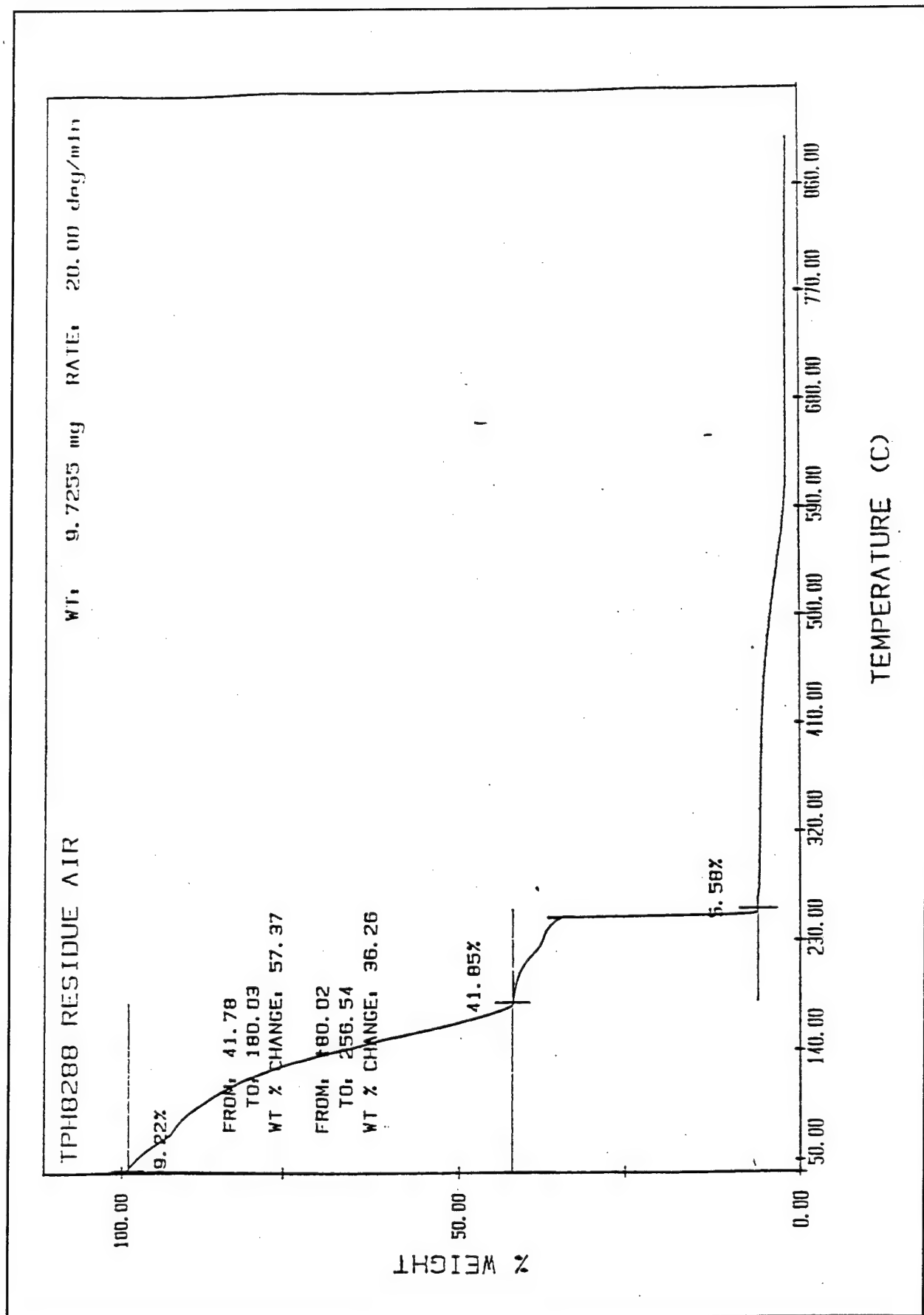


Figure 10. Sidewinder residue TGA trace, Test 1.

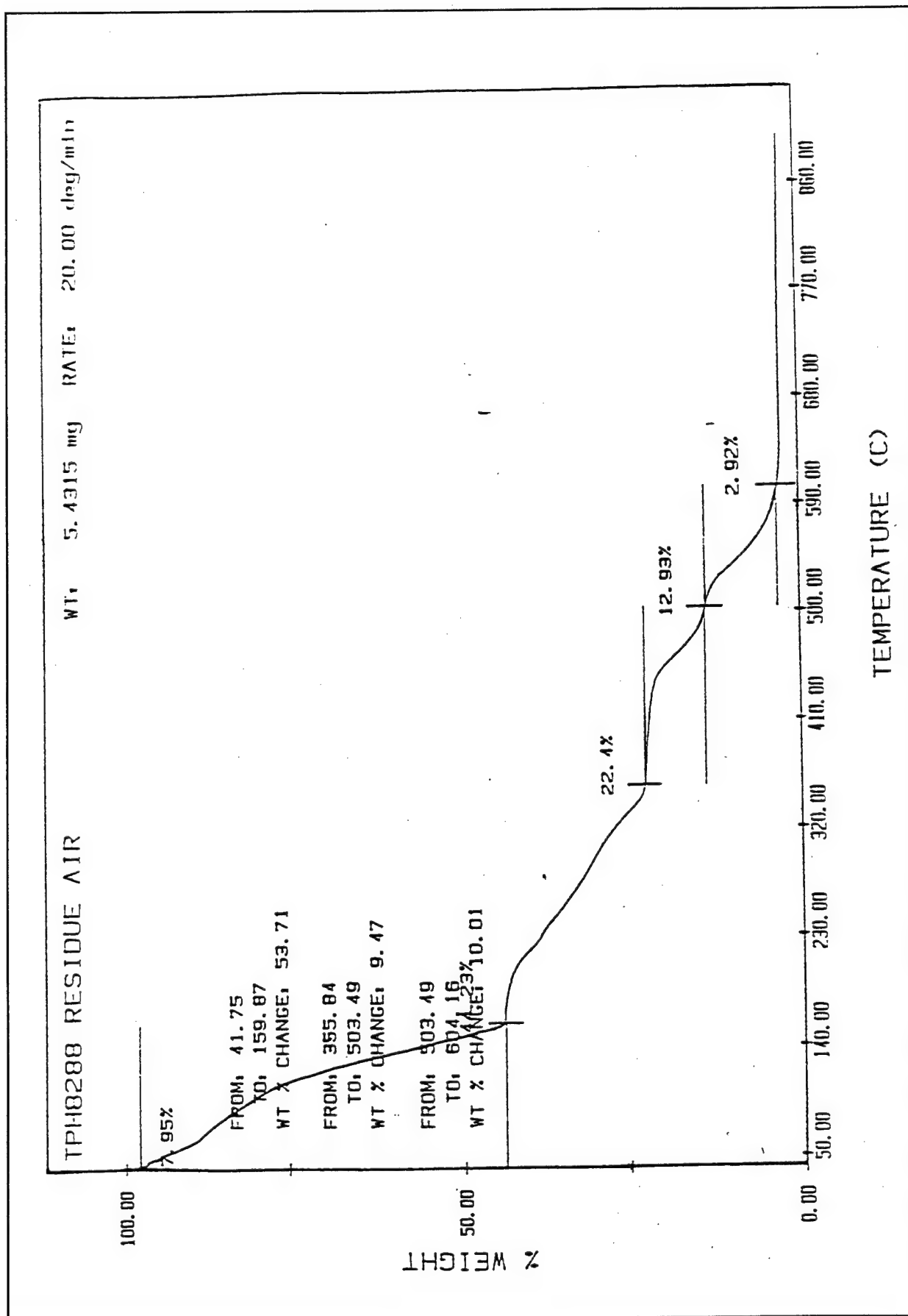


Figure 11. Sidewinder residue TGA trace, Test 2.

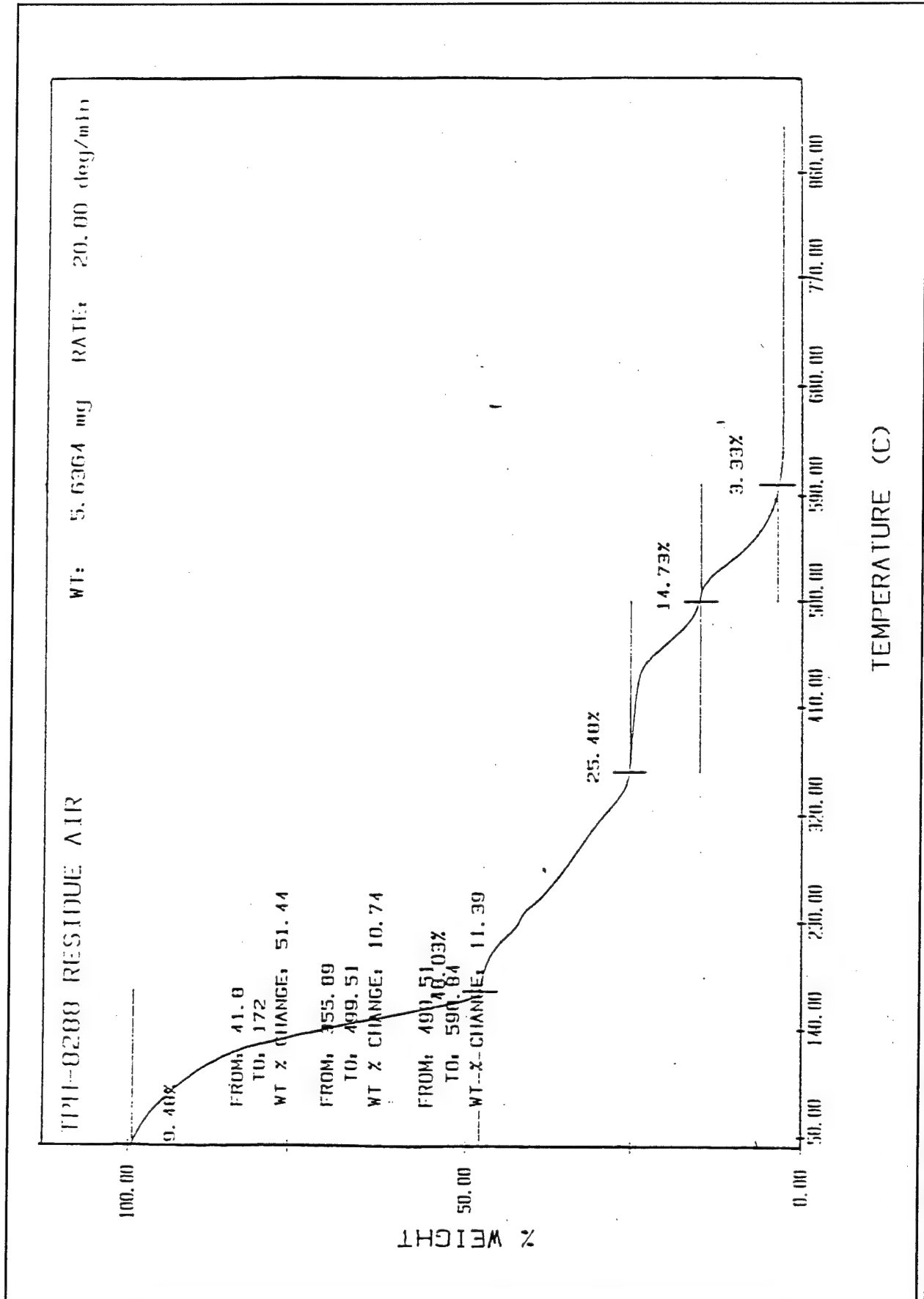


Figure 12. Sidewinder residue TGA trace, Test 3.

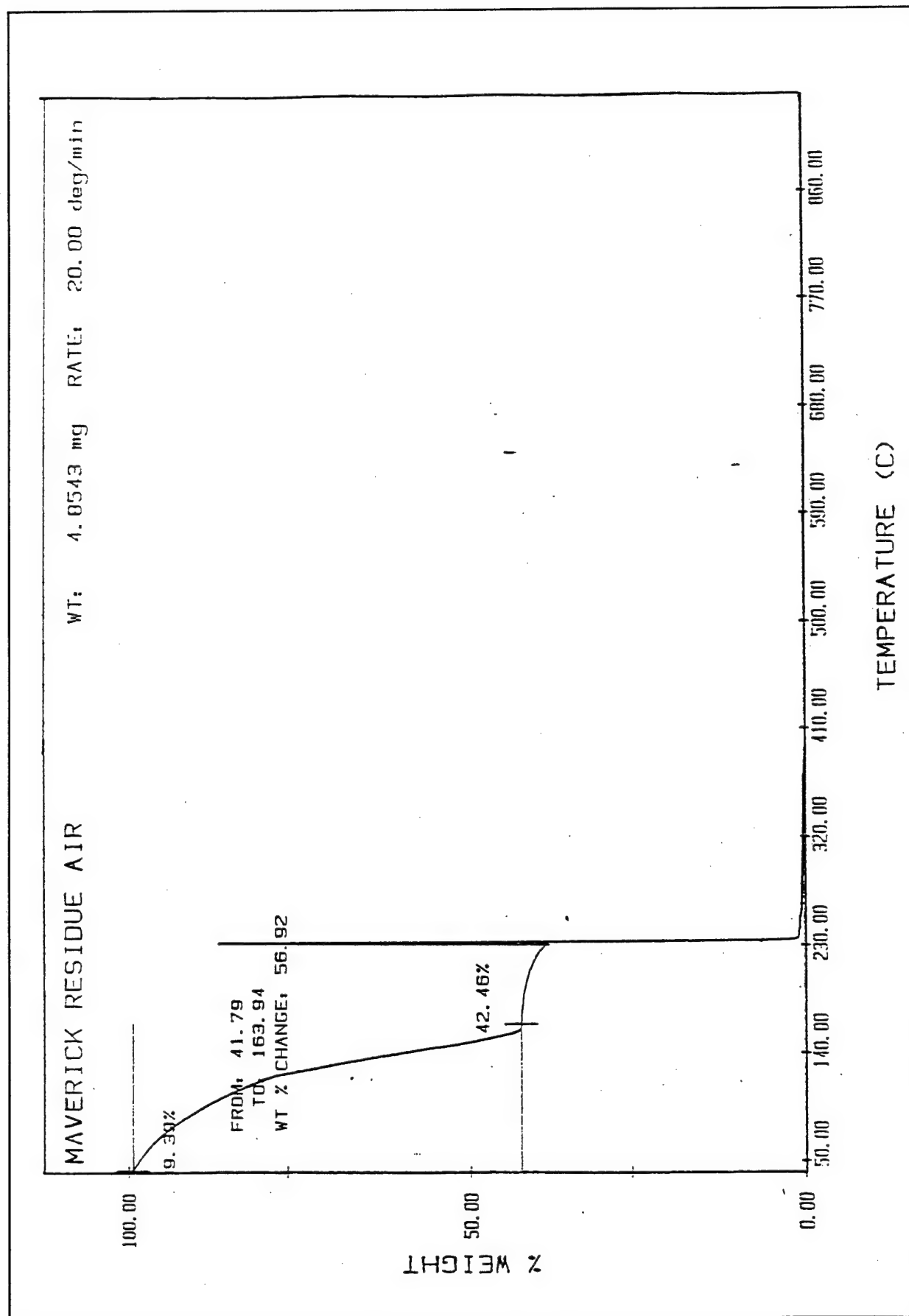


Figure 13. Maverick residue TGA trace, Test 1.

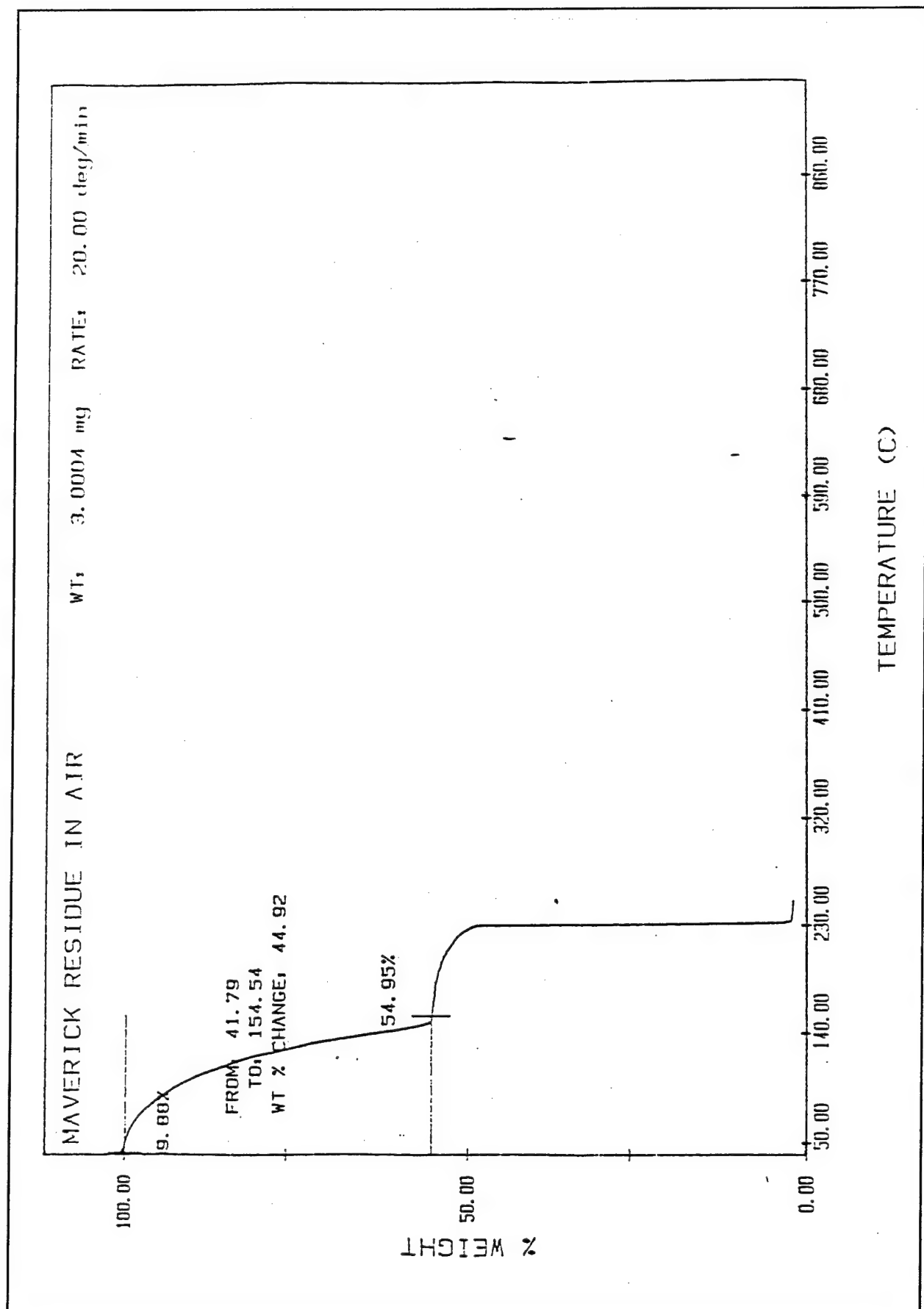


Figure 14. Maverick residue TGA trace, Test 2.

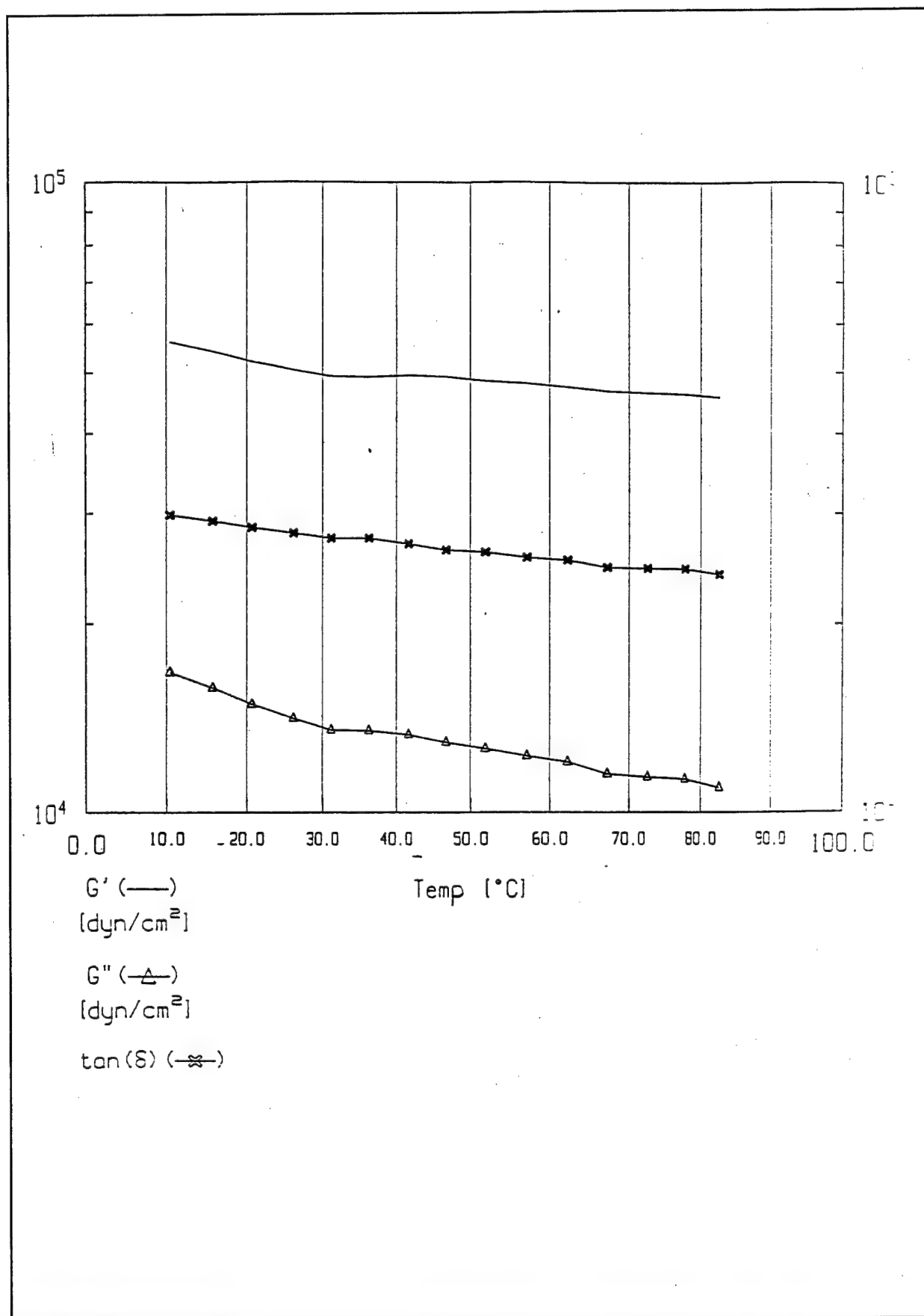


Figure 15. HARM residue RDS temperature sweep.

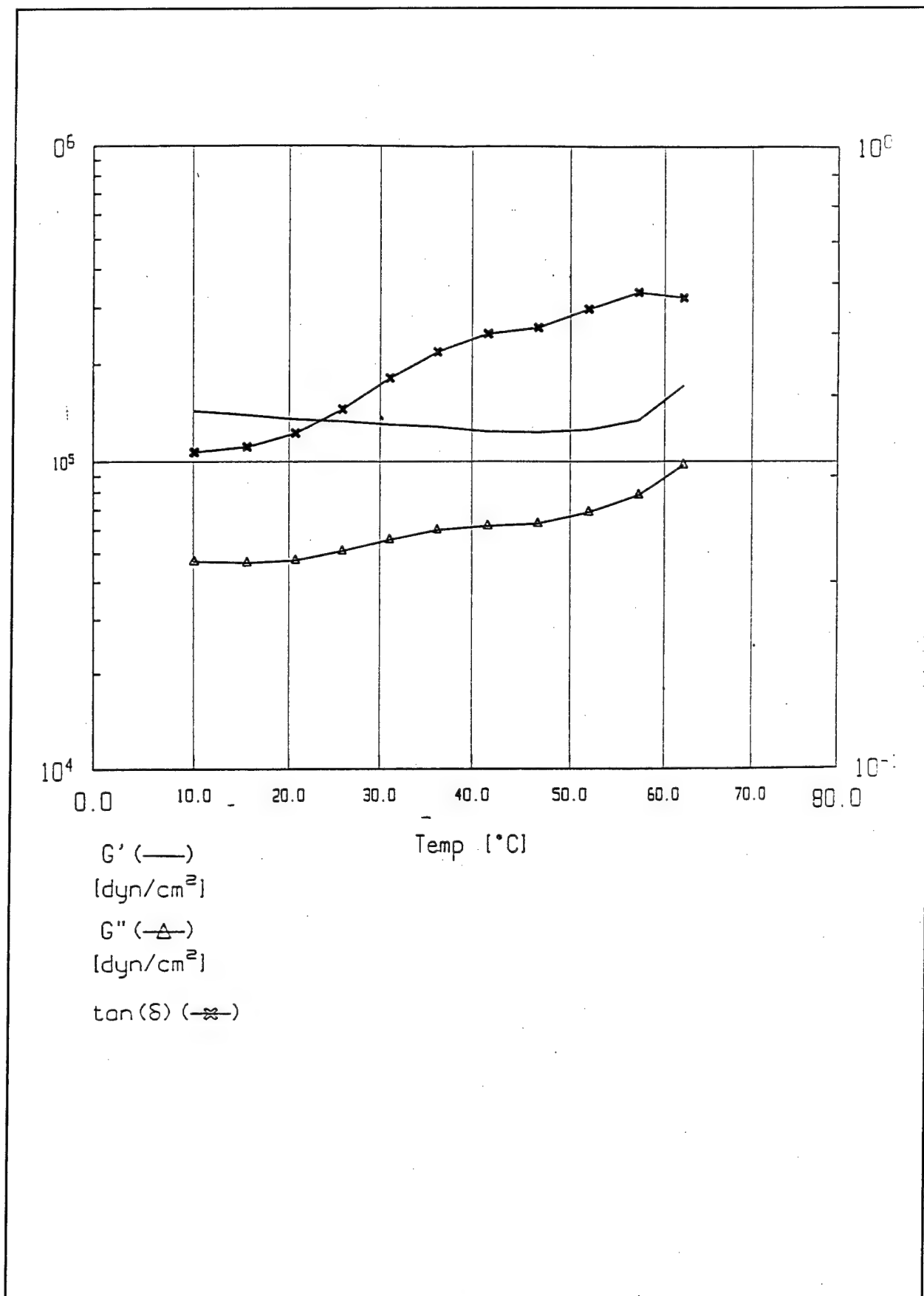


Figure 16. Maverick residue RDS temperature sweep.

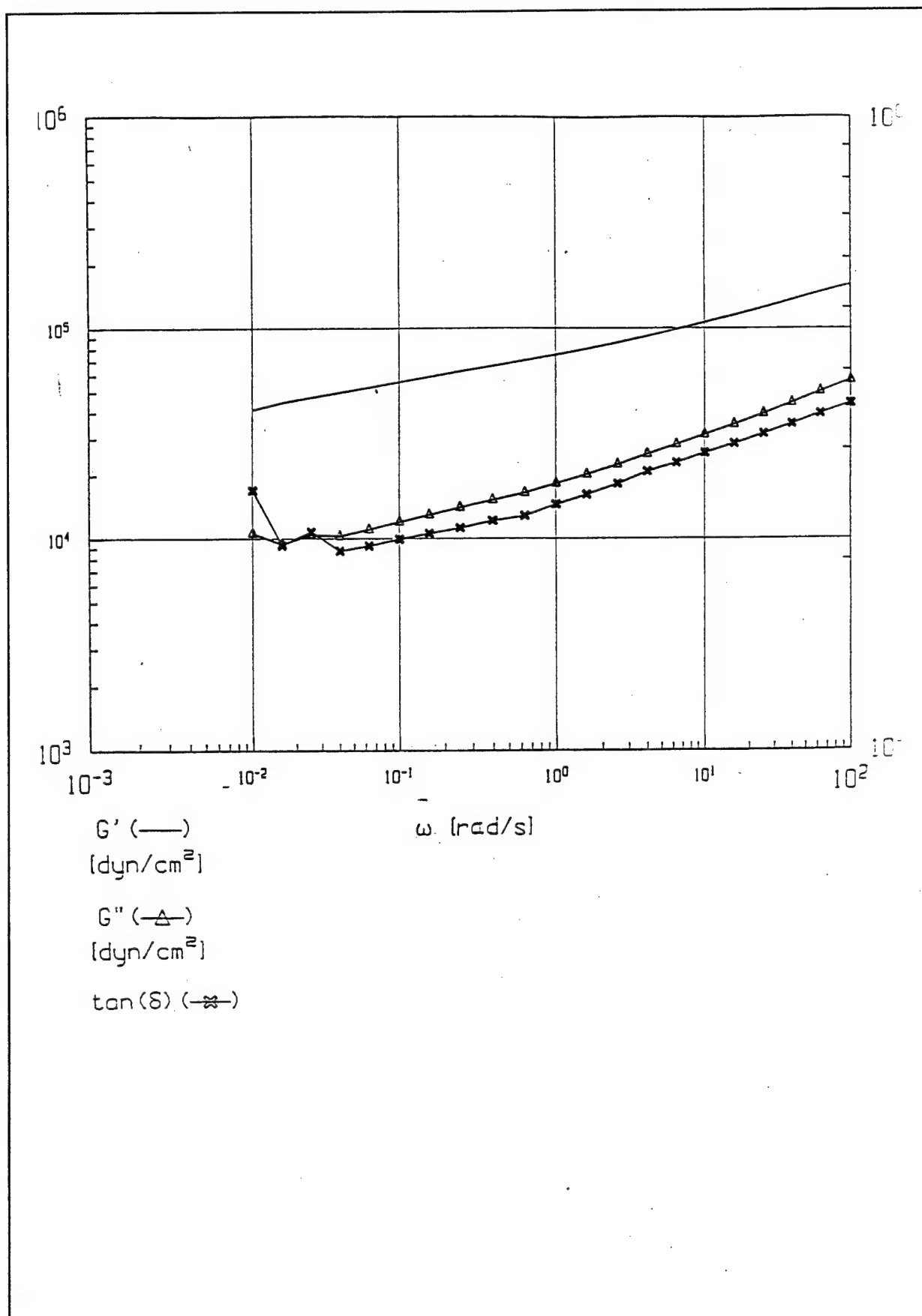


Figure 17. HARM residue frequency sweep.

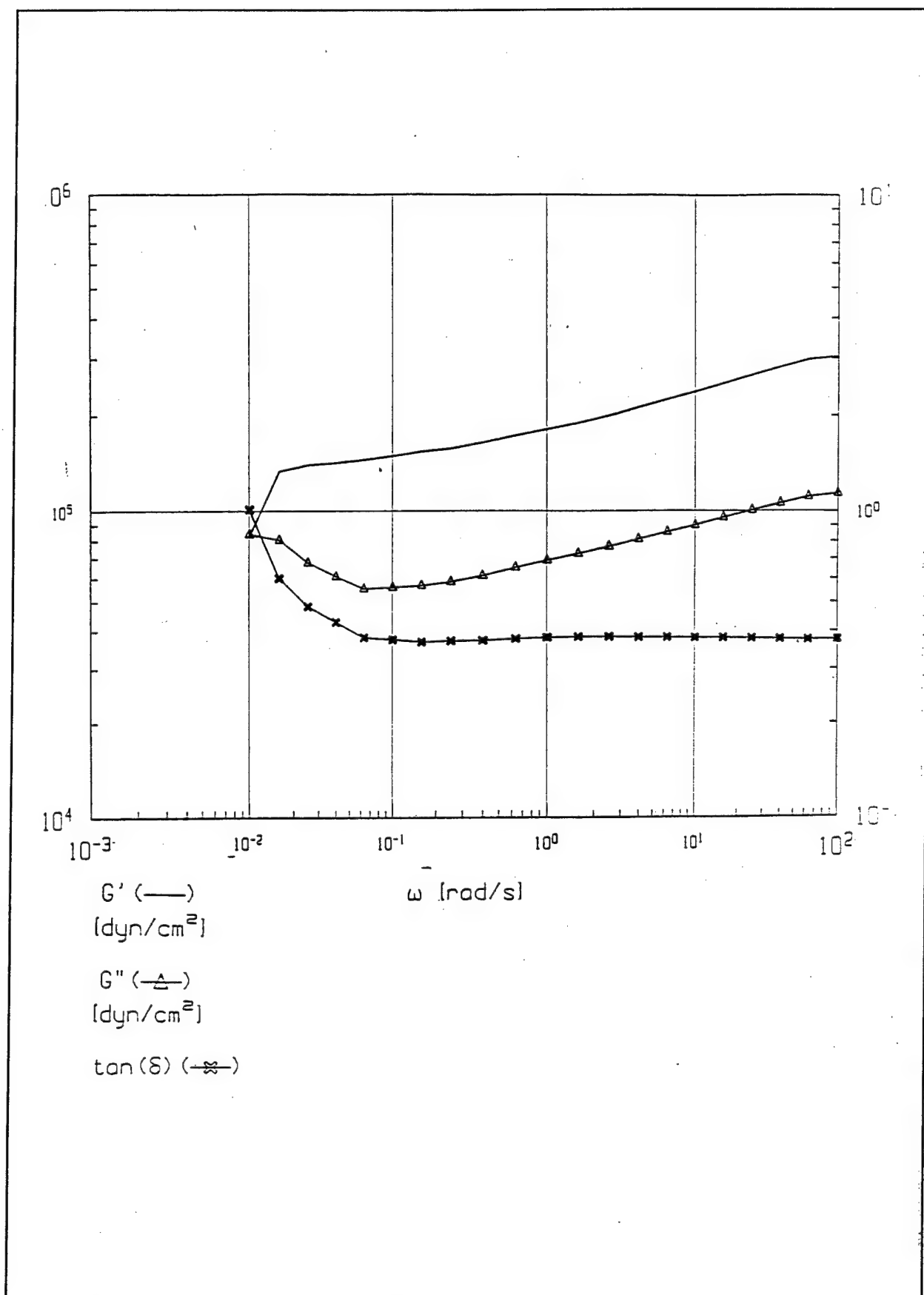


Figure 18. Maverick residue frequency sweep.

3 Bench-Scale Combustion Evaluation

Heat of Combustion

The heat of combustion was determined for each residue using a Parr Model 1241 oxygen bomb calorimeter with a Model 1720 calorimeter controller. The residues were tested at the moisture level present just after the reclamation process (i.e., without additional dewatering). Measurements were made at approximately 30 atmospheres oxygen pressure on samples ranging from approximately 0.25 to 0.90 g. Table 6 lists the test results. Values for other typical fuels (Brown and LeMay 1981) are shown for comparison.

Fuel Values

Fuel values obtained for the Sidewinder and Maverick propellant residues are considerably lower than the values for other common fuels. This difference is undoubtedly due to the high moisture level in these residues. The fuel value of the HARM residue is approximately equivalent to that of wood.

Table 6. Propellant fuel values.

Fuel	Approximate Elemental Composition (%)			Fuel Value (kJ/g)
	C	H	O	
HARM residue at 37% H ₂ O	46	9.5	38	15.3
Sidewinder residue at 62% H ₂ O	25	13	60	7.43
Maverick Residue at 62% H ₂ O	19	17	58	6.46
Wood (pine)	50	6	44	18
Anthracite coal	82	1	2	31
Bituminous coal	77	5	7	32
Charcoal	100	0	0	34
Crude oil	85	12	0	45
Gasoline	85	15	0	48
Natural gas	70	23	0	49

Thermochemical energy calculations were performed to determine the fuel value of the residues at incrementally lower moisture values. Two methods were used to calculate heat of combustion: (1) the NASA-Lewis program and (2) a method described in *Perry's Chemical Engineers' Handbook* (1984) for estimating solid fuel values. Table 7 summarizes these results. Pressure effects are assumed to be negligible. When comparing the calculated fuel values to the observed fuel values at the appropriate moisture level, the NASA-Lewis method appears to be more accurate. The NASA-Lewis method, which is designed to predict propellant combustion characteristics, is fairly accurate for the Maverick and Sidewinder residues (6.6 and 6.1 kJ/g predicted vs. 7.4 and 6.5 kJ/g observed), but significantly under-predicts for the HARM residue (8.8 kJ/g predicted vs. 15.3 kJ/g observed). The Perry's method, on the other hand, which is designed to predict fuel values for coal products, significantly over-predicts for each type of residue. Based on the NASA-Lewis calculations, it appears that complete dewatering would increase the residue fuel values between 15 and 57 percent. It is recommended that heat of combustion be determined on dried material (no water) to confirm these results.

Cost estimates for dewatering the binder residue are presented in Table 8. Costs are based primarily on direct labor for labor intensive unit operations, and are calculated according to the H.E. Wessel equation (Perry 1984). Reducing the moisture level to 20 percent appears feasible with additional processing using existing equipment. Capital expenditures would be required to obtain lower moisture levels (approximately \$200,000 to achieve 10 percent and \$250,000 to remove all water). Labor costs (for all three propellant residues) to obtain 10 percent moisture, are approximately equivalent to the costs to obtain 20 percent moisture, which is just under \$0.50/lb. Dewatering cost estimates will be used in conjunction with the fuel

Table 7. Calculated fuel value vs moisture level.

Residue Type	Moisture Level (%)	Perry Method Fuel Value (kJ/g)	NASA-Lewis Method Fuel Value (kJ/g)	Observed Fuel Value (kJ/g)
HARM	0	34.3	10.1	15.3
	10	31.3	9.8	
	20	28.2	9.5	
	37	23.1	8.8	
Maverick	0	25.9	9.9	7.4
	10	23.7	9.6	
	20	21.5	9.2	
	62	12.3	6.6	
Sidewinder	0	40.3	9.6	6.5
	10	36.7	9.2	
	20	33.1	8.8	
	62	17.8	6.1	

value vs. moisture level results to determine the cost/benefit of dewatering. This effort will be completed in Phase II of the project, once market for the residues values have been assessed.

To evaluate environmental liability associated with using the residues as commercial fuel sources, the gaseous and solid combustion products were analyzed. Analyses included IC, gas chromatography/mass spectroscopy (GCMS), cyanide, and ICP-atomic emission spectroscopy (ICP-AES) (Alpisa 1994; Bates and Dearden 1994). For the IC analyses, HARM, Sidewinder, and Maverick propellant residues were dried overnight in a 105 °C forced-air oven to remove excess moisture. Two dried samples per residue were burned in a Parr bomb under 30 atmospheres of oxygen. The IC samples were burned over 20 ml of IC eluent. After combustion, the bomb was cooled and the eluent was filtered. The filtrate was analyzed by IC. Results are presented in Table 9 and are reported as percentages based on the original samples. Values for hydrogen chloride (HCl) content, as measured by percent Cl, are close to what is theoretically predicted based on the residue compositions (measured 2.9, 14.9, and 2.6 percent vs. predicted 2.0, 10.5, and 1.9 percent for HARM, Maverick, and Sidewinder residues, respectively).

Values for HNO_3 and NO_x are reported as percent N and are shown in Table 10. The measured values are well below the maximum possible based on the residue elemental analyses, indicating that most of the available nitrogen is converted to N_2 .

Table 9. Gaseous combustion products.

Propellant Residue	Cl (%)	N (%)	Cyanide (ppm)	Benzene (ppm)
HARM	2.9	1.7	3.5	1.35
Sidewinder	2.6	1.0	3.1	ND
Maverick	14.9	1.2	2.4	ND
Note: Concentrations based on propellant residue before combustion.				

Table 10. Values for HNO_3 and NO_x as percent N.

Propellant Residue	Measured N (%)	Available N (%)	N Converted to N_2 (%)
HARM	1.7	8.6	80
Sidewinder	1.0	7.5	87
Maverick	1.2	4.8	75

As expected, fluoride was detected in the Maverick residue combustion products. Quantifying the fluoride level was not possible, however, because the fluoride peak occurred immediately after the void volume (retention time (RT) = 1.03 minutes) and because the filtrates were diluted to optimize chloride analyses. It is reasonable to assume that all of the fluoride present in the residue is converted to $\text{HF}_{(g)}$ during combustion.

The samples for GCMS analyses were combusted over 25 ml

of distilled deionized (DI) water followed by immediate removal of the gases. The gas was vented directly from the bomb into Tedlar bags. Benzene in the HARM propellant residue was detected at 1 ppm, which is near the method detection limit. An unknown compound was detected at an RT of 13.4 min in the Sidewinder propellant residue. The best MS library match is with n,n-dimethylacetamide (90 out of 100 match). The concentration is estimated at approximately 50 ppm. No organics were detected in the Maverick propellant residue combustion gases.

The samples for cyanide analyses were combusted over 10 ml of sodium hydroxide (NaOH). The combustion gases were also bubbled through NaOH. The caustic solution was distilled and analyzed colorimetrically for cyanide. The results in Table 9 show low levels of cyanide at concentrations close to the method detection limit. Although quantitation is imprecise at these low levels, it appears that trace amounts of cyanide are present in the propellant residues' combustion gases.

To determine the amount of ash residue after combustion, dried propellant residue (overnight at 105 °C) was combusted at 900 °C under ambient atmosphere for 2 hr. Results based on duplicate runs are shown in Table 11. Percentages are based on the original dry residue. The results correlate well with what is theoretically predicted based on the residue composition and indicate that very little ash remains after combustion.

To determine ash composition, the ashes were treated with a mixture of nitric and hydrochloric acid to solubilize any metals present. The digestion was not complete. Very small amounts of insoluble material were recovered during filtration of each sample. An ICP-AES technique was used to analyze the prepared solutions for the following metals:

Al - aluminum	Cu - copper	Sb - antimony
As - arsenic	Fe - iron	Se - selenium
Ba - barium	Mg - magnesium	Si - silicon
Be - beryllium	Mn - manganese	Sn - tin
B - boron	Mo - molybdenum	Sr - strontium
Cd - cadmium	Na - sodium	Tl - thallium
Ca - calcium	Ni - nickel	V - vanadium
Cr - chromium	P - phosphorus	Zn - zinc
Co - cobalt	Pb - lead	

Results, based on duplicate runs, are presented in Table 12. Results and detection limits are based on the ash residue mass (after combustion) and not on the original

mass of the propellant binder residue (before combustion). Elements not reported, if present, would be found in concentrations of less than 100 ppm.

Reasonable agreement was found for replicate determinations for the Sidewinder and Maverick residue ashes. More variance was observed in the HARM residue ash. This variance is partially a function of the small ash mass. Furthermore, it is likely the uncertainty is greater in the accuracy of the results because of the small ash weights.

Table 11. Ash residue after combustion.

Propellant Residue	Ash (%)	Predicted (%)
HARM	2.9	2.1
Sidewinder	2.3	2.2
Maverick	2.5	2.3

The HARM ash consists primarily of tricalcium phosphate (TCP) and aluminum oxide (Al_2O_3). The TCP level is approximately 23 percent of the ash. The Al_2O_3 level is likely higher than what is calculated from the aluminum value (39 percent Al_2O_3). Based on the initial 0.2 percent Al_2O_3 present in HARM propellant, and assuming all of the Al_2O_3 remains with the residue, 52 percent Al_2O_3 is expected to be in the

Table 12. Combustion ash analysis.

Element	HARM Residue Ash	Sidewinder Residue Ash	Maverick Residue Ash
Al	20.82%	973 ppm	2.53%
Ba	114 ppm	48 ppm	234 ppm
B	2145 ppm	645 ppm	956 ppm
Ca	8.51%	4.19%	4.53%
Cr	141 ppm	124 ppm	263 ppm
Cu	79 ppm	128 ppm	201 ppm
Fe	0.597%	982 ppm	11.95%
Mg	0.361%	726 ppm	1195 ppm
Mn	270 ppm	ND	479 ppm
P	5.67%	2.05%	1.95%
Si	3.559%	1604 ppm	0.374%
Na	0.590%	0.230%	0.296%
Sr	68 ppm	13 ppm	22 ppm
Zn	859	1008 ppm	0.337%
Total (%)	40.47%	7.10%	22.30%

ash. The analytical method is low because Al_2O_3 is not completely soluble with the ICP digestion method.

The Sidewinder ash consists primarily of zirconium carbide (ZrC) and TCP. Although ZrC is insoluble and therefore not detectable with ICP, the propellant composition and ash mass balance indicate that approximately 86 percent of the ash is ZrC.

The Maverick ash consists primarily of ZrC, ferric fluoride, TCP, and Al_2O_3 . As with the Sidewinder ash, the ZrC level in the Maverick ash is calculated to be approximately 55 percent.

4 Pilot-Scale Combustion Evaluation

Pilot-scale rotary kiln and spreader stoker tests were conducted on the HARM residue by the University of Utah, Department of Chemical and Fuels Engineering. The rotary kiln testing evaluated the residue at three moisture levels and two rotation rates. The kiln was operated in a batch mode. The residue was co-fired with coal in the spreader stoker. Testing was designed to see if the nitric oxide (NO) concentrations could be reduced by staging the combustion. The spreader stoker was operated in a continuous mode.

Tests were performed to characterize the emissions from the combustion of HARM, nonaluminized propellant binder residue. The tests were also performed to determine if the residue could be used as a fuel. The residue was burned in two pilot-scale facilities: a batch, 100,000 Btu/hr rotary kiln and a continuous, 10^6 Btu/hr spreader stoker. The tests performed in the kiln were qualitative in nature. The kiln was maintained at 1,400 °F and was rotated at 0 and 0.5 rpm. Fifty-gram samples of the residue were tested at three moisture levels, 37, 30, and 15 weight percent. Flue gas levels of oxygen (O_2), carbon dioxide (CO_2), and NO were continuously monitored. The combustion of the residue was well behaved and was similar to that of coal.

The tests performed in the stoker were designed to see if the NO concentrations could be reduced by staging the combustion. Bed region stoichiometric ratios of 1.5, 1.25, 1.00, 0.90, and 0.78 were examined. Stoichiometric ratio is the ratio of the number of moles of air supplied to the system to the number of moles of air required for complete combustion. The residue was co-fired with coal at the rates of 44 lbm/hr coal and 12 lbm/hr residue. A 37 percent reduction in NO emissions was achieved using a bed-region stoichiometry of 0.78.

Experimental Facilities

The small, pilot-scale rotary kiln used in this study is shown schematically in Figure 19. A detailed description of the kiln can be found in Owens (1991). The 130-kW facility is fired with natural gas and the exhaust gases exit to a 100-kW secondary combustion chamber. In these tests, the secondary chamber was not used. The

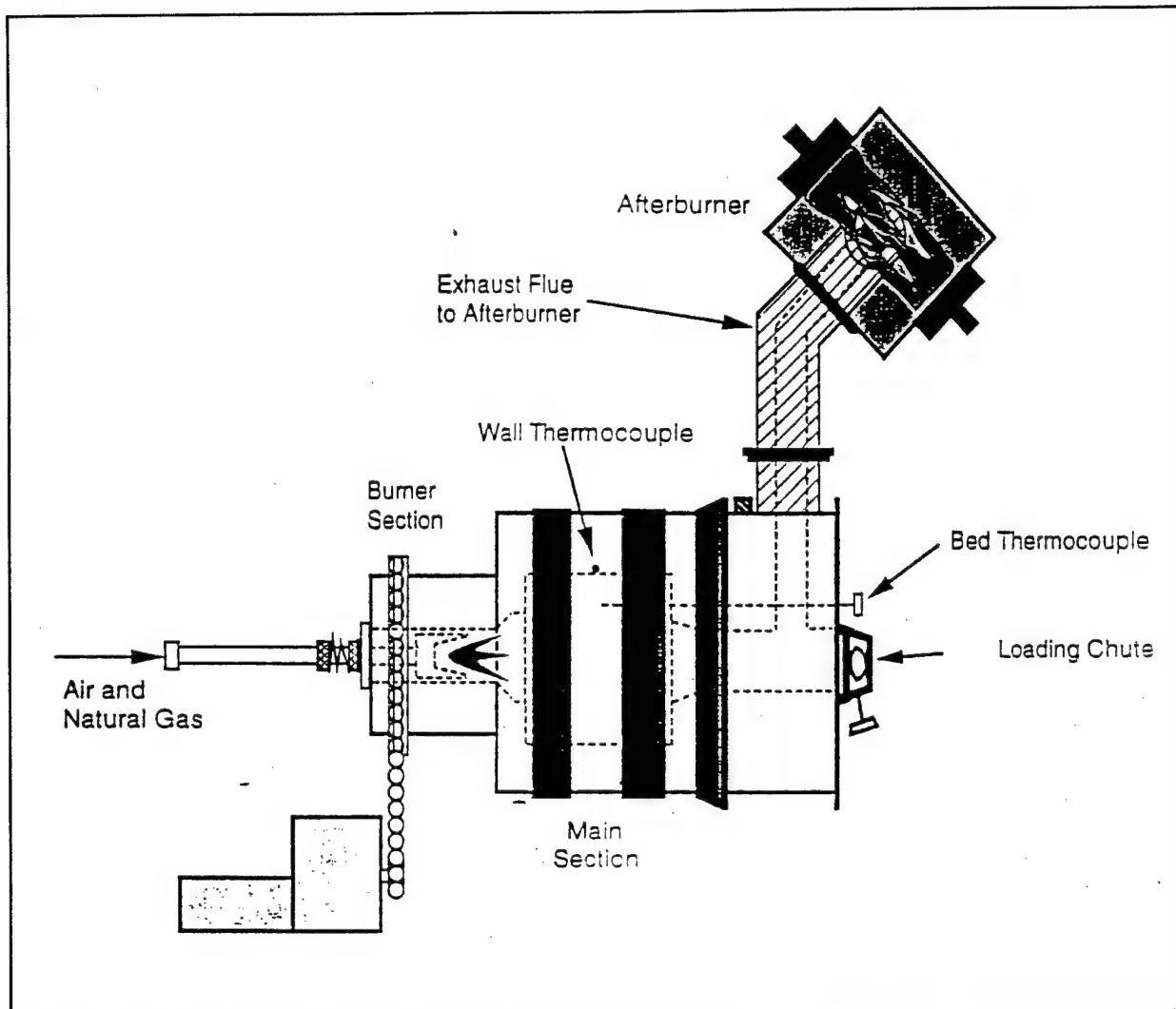


Figure 19. Schematic of small, pilot-scale rotary kiln and afterburner.

inside dimensions of the kiln are 61-by-61 cm. The kiln is batch in nature and time in the kiln corresponds to distance from the feed end in a continuous facility. The residue was fed through the loading chute in roughly 50-g lumps. The same loading chute was used for video recordings of the experiment. The temperature of the gas near the center of the kiln was measured with a suction pyrometer. The temperature of the wall was measured with thermocouples embedded in the refractory lining of the kiln. They extended to within 1 cm of the inner surface of the wall.

The pilot-scale spreader stoker is shown schematically in Figure 20. The stoker consists of seven vertical and one horizontal sections. The total height of the stoker is 10.5 ft, and the area of the grate is 1 sq ft. The stoker was designed to be fired at rates from 0.5 to 1 million Btu/hr. Air is injected below the grate (under-fire air) and at adjustable locations above the grate (over-fire air). The over-fire air port used in these experiments is indicated in Figure 20. Coal was fed to the facility from a

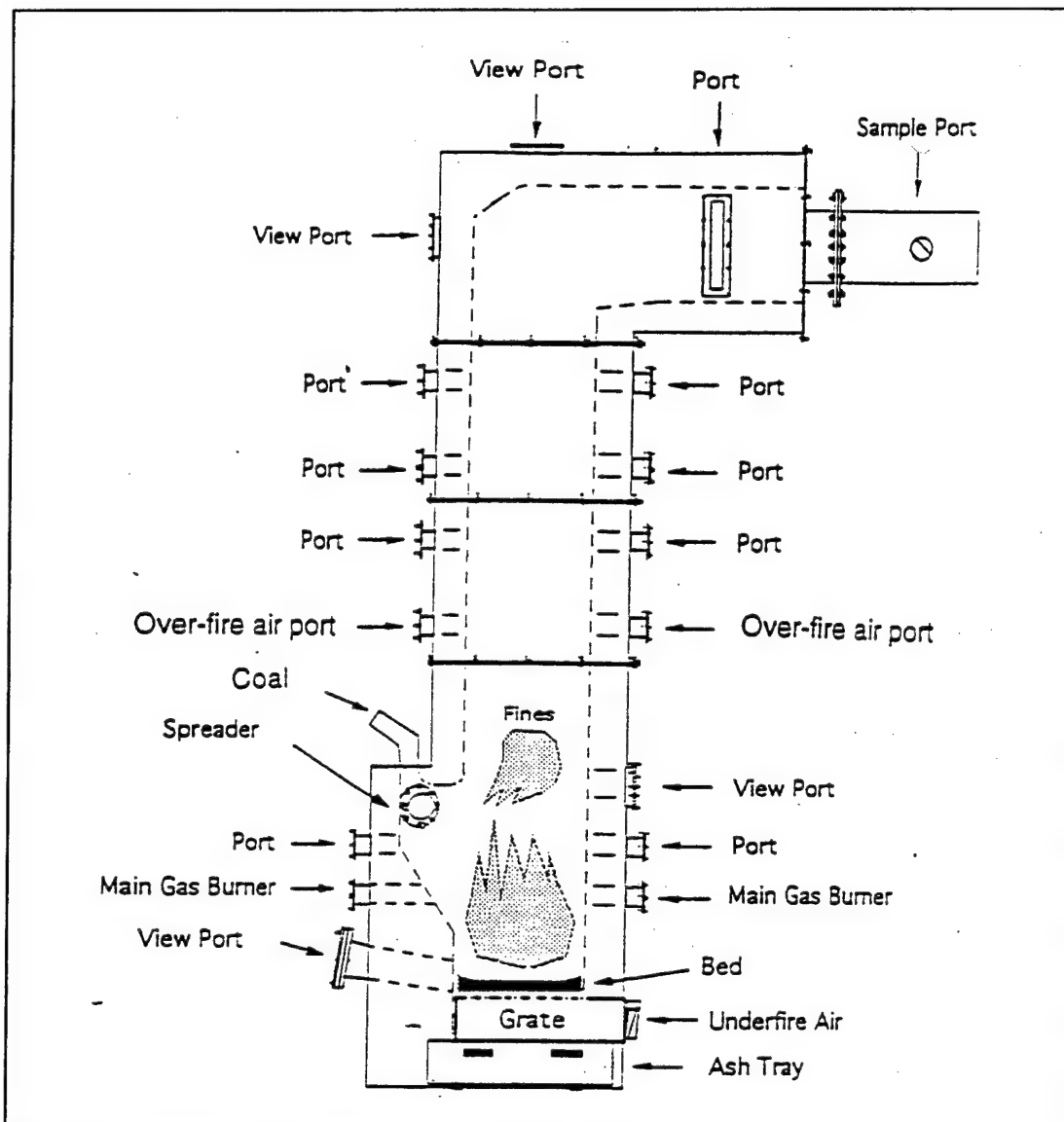


Figure 20. Schematic of pilot-scale spreader stoker facility.

hopper on the floor above. The residue was fed by hand through a chute attached to the main coal chute. The spreader is located 32 in. above the grate, in agreement with commercial practice, and it flings the fuel out uniformly over the grate.

Rotary Kiln Results and Discussion

The conditions for the six experiments performed in the rotary kiln are summarized in Table 13. The samples of residue for runs 18 to 21 were dried in an electrically heated oven at 122 °C. The "as-received" composition of the HARM residue is given in Table 14. The moisture level is 37 weight percent and on a dry basis the nitrogen content is 8.57 percent. The nitrogen is present as AP and as organic compounds.

Table 13. Conditions for rotary kiln tests.

Run	Kiln Wall Temp. (°F)	Kiln Gas Temp. (°F)	Kiln Rotation Rate, (rpm)	Sample Weight Before Drying (g)	Sample Weight After Drying (g)	Sample Drying Temp. (°C)	Sample Drying Time (hr)	Sample Wt % Water
16	1375	1403	0	53.3	-	-	0	37.0
17	1390	1437	0.5	53.4	-	-	0	37.0
18	1372	1398	0	52.0	46.6	122	1	29.7
19	1383	1430	0.5	55.7	50.3	122	1	30.2
20	1377	1412	0	57.4	42.4	122	3	14.7
21	1380	1415	0.5	54.1	40.6	122	3	16.1

The heat of combustion of the residue, on an as-received basis, is 3,600 cal/g or 6,480 Btu/lbm.

The kiln was maintained at roughly 1,400 °F and was rotated at 0 and 0.5 rpm. The baseline oxygen concentration in the kiln's exit gases, in the absence of residue combustion, was roughly 12 percent by volume on a dry basis. Fifty-gram samples of the residue were tested at three moisture levels, 37, 30, and 15 weight percent. Roughly cubical lumps of sample were fed into the kiln singly in a batch fashion. Flue gas levels of O₂, CO₂, and NO were continuously monitored and are reported here on an as-measured, dry basis. Only the concentrations of O₂ and NO are given. The combustion of the residue was well behaved and was similar to that of coal.

The O₂ traces for runs 16, 18, and 20, during which the kiln was not rotated, are shown in Figure 21. The O₂ traces for runs 17, 19, and 21, during which the kiln was rotated at 0.5 rpm, are shown in Figure 22. In all of the oxygen traces, the early spike in the O₂ level is due to opening the loading chute for sample feeding. Comparing Figures 21 and 22 shows no apparent effect of kiln rotation on combustion rate because of the nature of the sample, which was a single lump of residue. If many pieces of residue were fed into the kiln, the rotation rate would have an effect on the combustion rate. The effect of sample moisture content is much more obvious. The drier samples burned more rapidly, with oxygen concentrations falling as low as 4 percent. It took roughly 10 minutes for the samples to be reduced completely to ash. Little ash was observed.

Table 14. Composition of HARM propellant residue.

Moisture (%)	37
AP	6.61
C	72.98
H	8.50
N	8.57
O	7.43
Cl	2.00
ash	0.52
Total	100.00

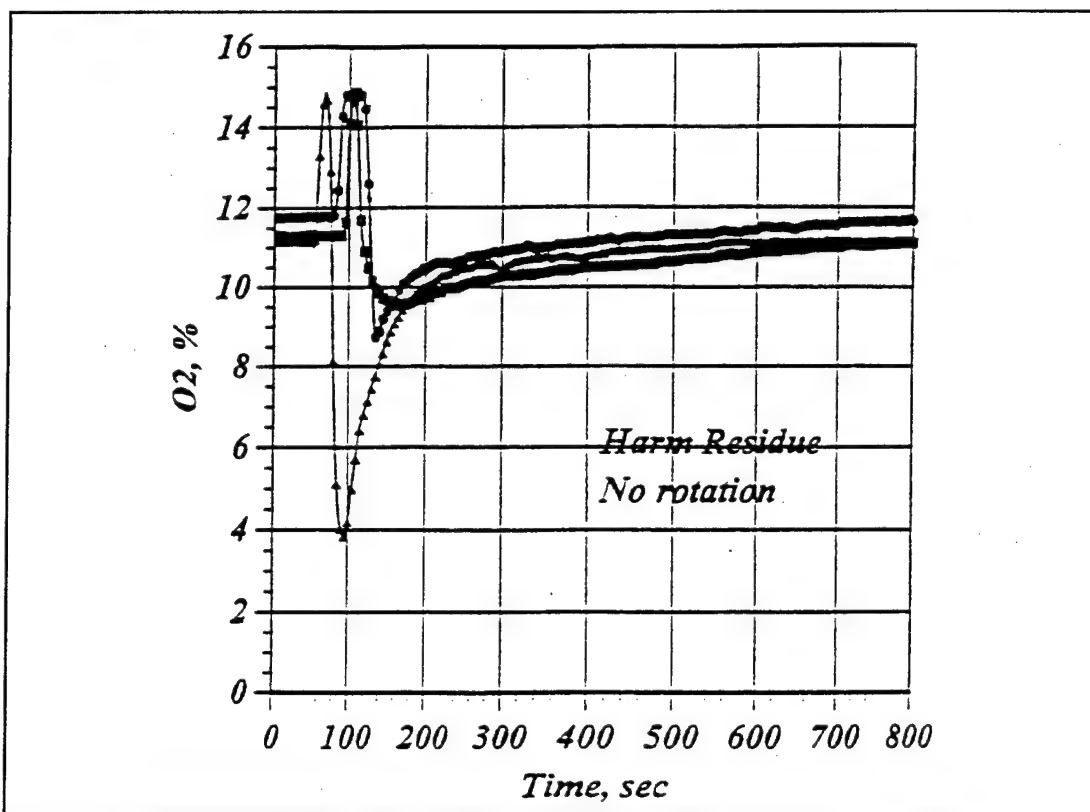


Figure 21. Oxygen traces for the HARM residue in the rotary kiln at 0 rpm.

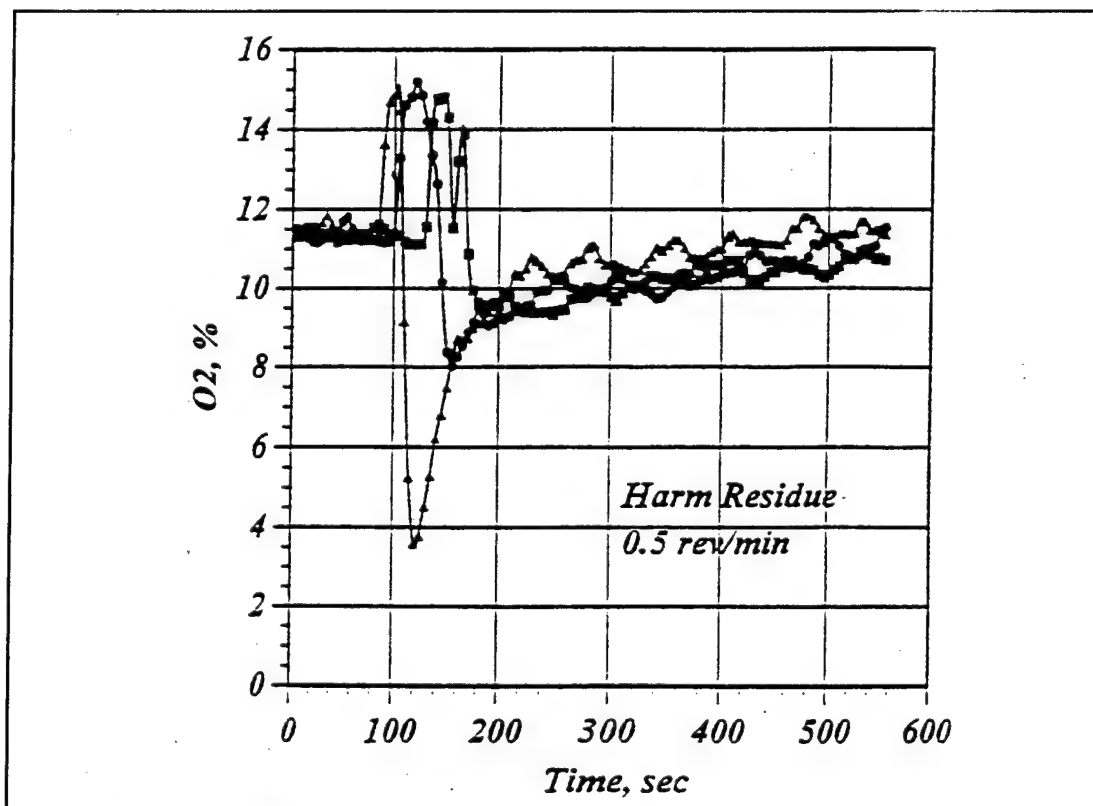


Figure 22. Oxygen traces for the HARM residue in the rotary kiln at 0.5 rpm.

Based on visual observations of the driest samples (runs 20 and 21), the oxygen in the bottom half of the kiln was completely consumed, and no flames were visible there. In all other cases, flames were attached to the residue almost immediately after it was dropped in the kiln. The dry samples burned faster because they heated up faster.

The corresponding NO traces are shown in Figures 23 and 24 on a dry, as measured basis. The baseline NO concentration from the natural gas flame is 25 ppm. The addition of residue to the kiln caused a large increase in the NO levels. NO was released over the roughly 10 minutes that it took for the samples to completely burn. The moisture content of the sample had a pronounced effect on the rate of NO production, which corresponds to the effect of moisture on the rate of combustion. The dry samples produced NO at a much higher rate than the wet samples, although the total amount of NO released for the different moisture content samples appeared to be roughly the same. The dry samples produced most of their NO quickly while the wet samples produced their NO more gradually.

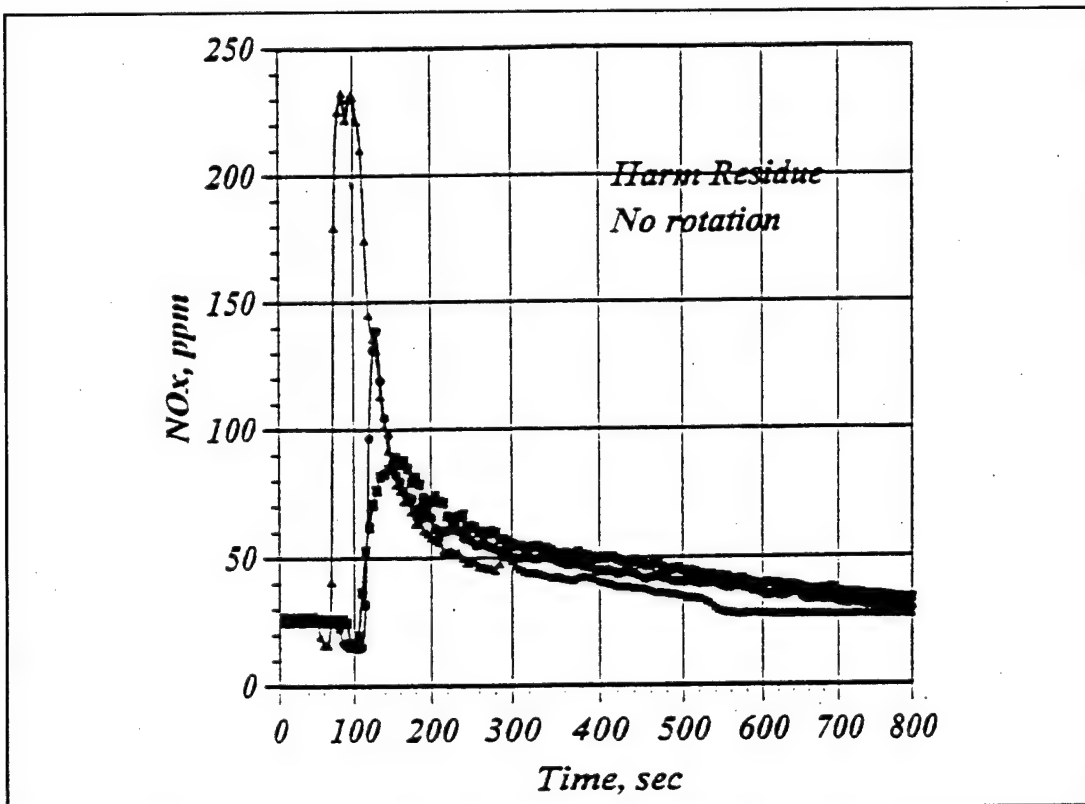


Figure 23. Nitric oxide traces for the HARM residue in the rotary kiln at 0 rpm.

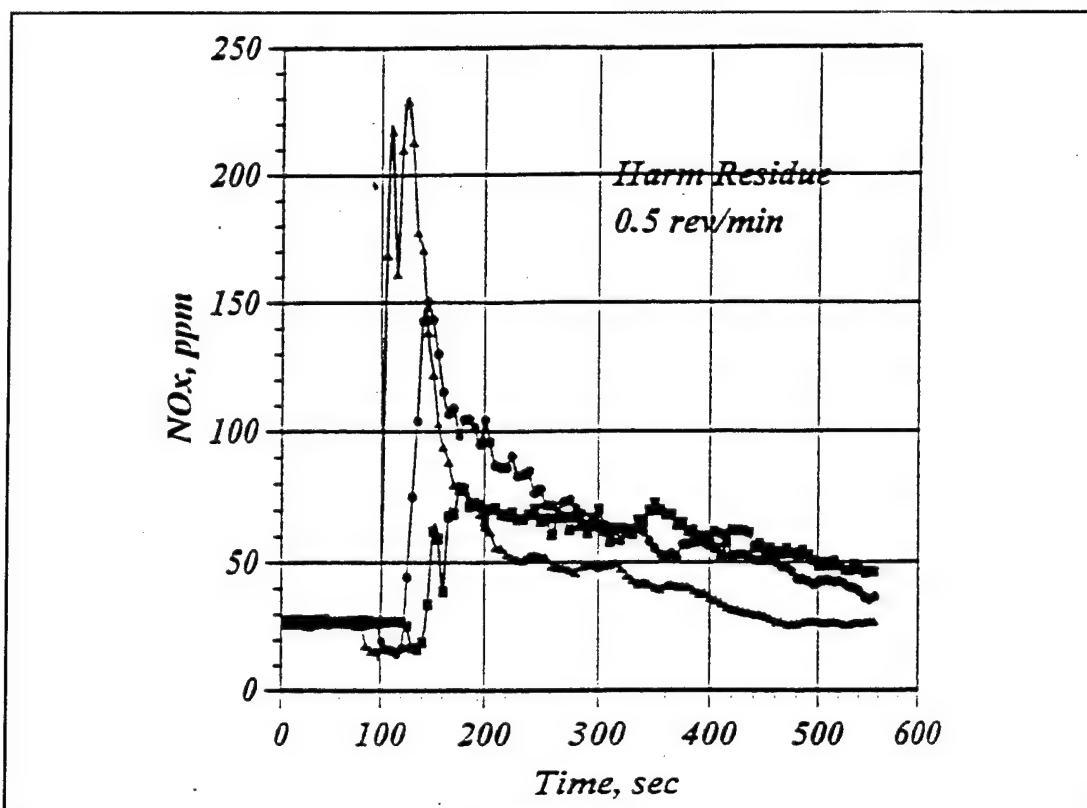


Figure 24. Nitric oxide traces for the HARM residue in the rotary kiln at 0.5 rpm.

Spreader Stoker Results and Discussion

The tests performed in the spreader stoker were designed to see how far NO concentrations could be reduced by staging the combustion. Conditions for the five experiments performed in the stoker are summarized in Table 15. Bed region stoichiometric ratios of 1.5, 1.25, 1.00, 0.90, and 0.78 were examined. Stoichiometric ratio is defined as the ratio of the number of moles of air supplied to the system to the number of moles of air required for complete combustion. The overall stoichiometric ratio was fixed at 1.5. The coal and residue were fed into the stoker at rates of 44 lbm/hr and 12 lbm/hr. The residue was fed in every 15 sec in roughly 22-g lumps. Table 16 gives the composition of the coal. The heating value of the coal on an as-received basis is 12,500 Btu/lbm.

To establish a basis for comparison, flue-gas concentrations of NO, CO₂, and O₂ were recorded while burning coal alone at the rate of 44 lbm/hr with a bed region stoichiometry of 1.5. These measurements are shown in Figure 25 on a dry, as-measured basis. The NO levels for coal alone were about 270 ppm.

The flue-gas concentrations of O_2 for all of the coal-HARM experiments are shown in Figure 26 on a dry, as-measured basis. The O_2 concentrations average about 7 percent. The corresponding NO concentrations are given in Figure 27, again on a dry, as-measured basis. The NO data show the expected decrease in NO with decreasing bed-region stoichiometric

ratio. The NO concentrations at a bed-region stoichiometry of 1.5 are about 430 ppm versus 270 ppm for the coal-only case shown in Figure 25. The NO concentrations at a bed-region stoichiometry of 0.78 are about 270 ppm which, compared with 430 ppm, is a reduction of 37 percent. The NO data shown in Figure 27 are replotted in Figure 28 on a dry basis and at 3 percent O_2 . This replotting causes the NO concentrations in Figure 28 to appear

Table 15. Conditions for spreader stoker experiments.

Run	Average Stoker Bed Region Temp. (°F)	Overall Stoichiometry	Bed Region Stoichiometry
1	2283	1.5	1.5
2	2352	1.5	1.25
3	2364	1.5	1.00
4	2369	1.5	0.90
5	2406	1.5	0.78

Table 16. Composition of coal.

C	71.80
H	6.03
N	1.24
O	10.79
S	0.36
ash	9.78
Total	100.00

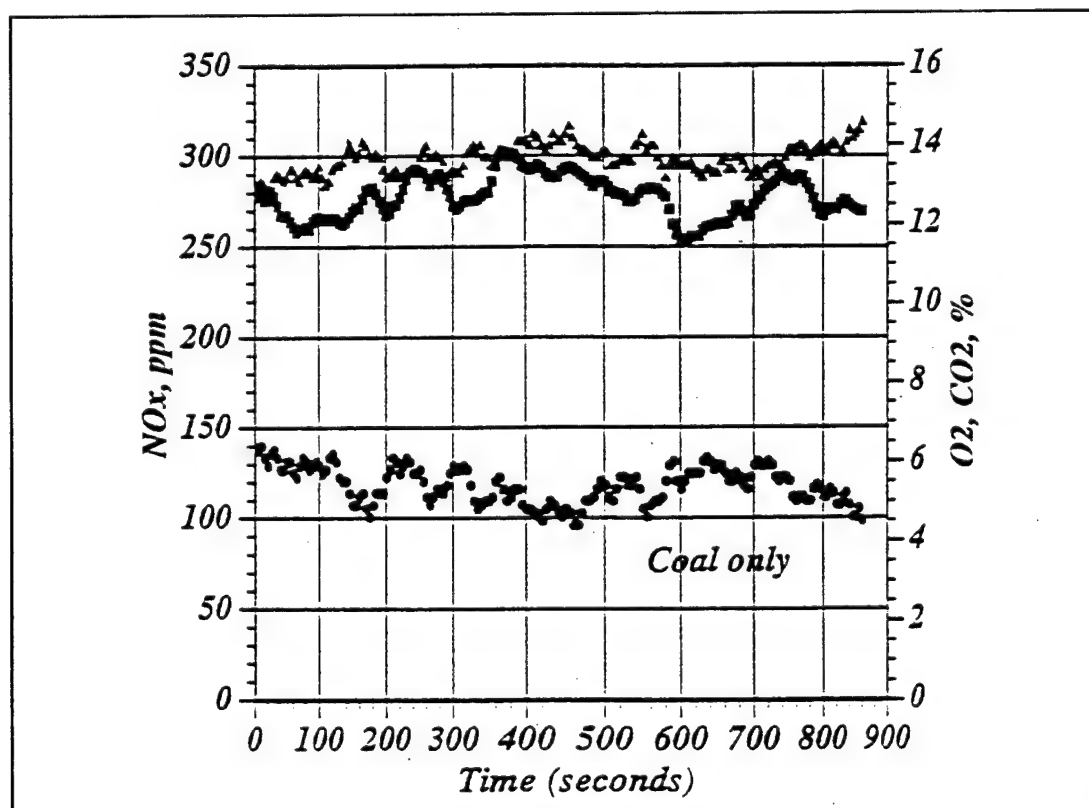


Figure 25. Nitric oxide, oxygen, and carbon dioxide traces for a coal-only test in the spreader stoker.

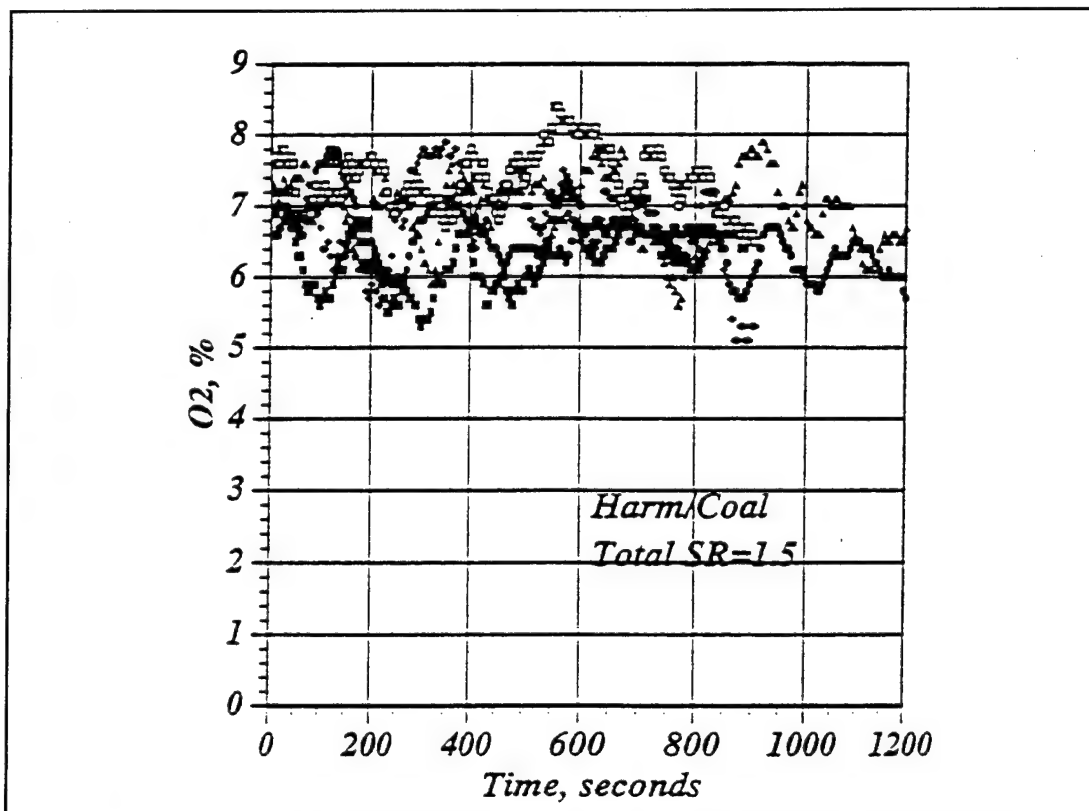


Figure 26. Oxygen traces for bed-region stoichiometric ratios for the cofiring of coal and residue in the spreader stoker.

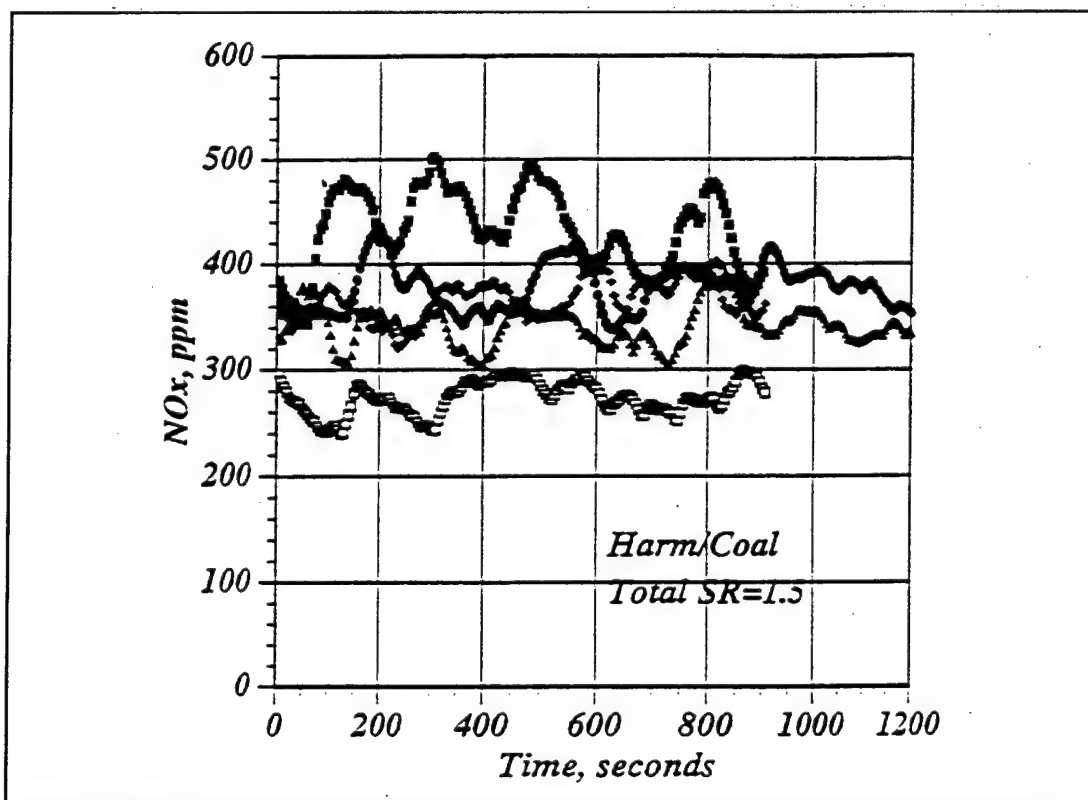


Figure 27. Nitric oxide traces for bed-region stoichiometric ratios for the cofiring of coal and residue in the spreader stoker.

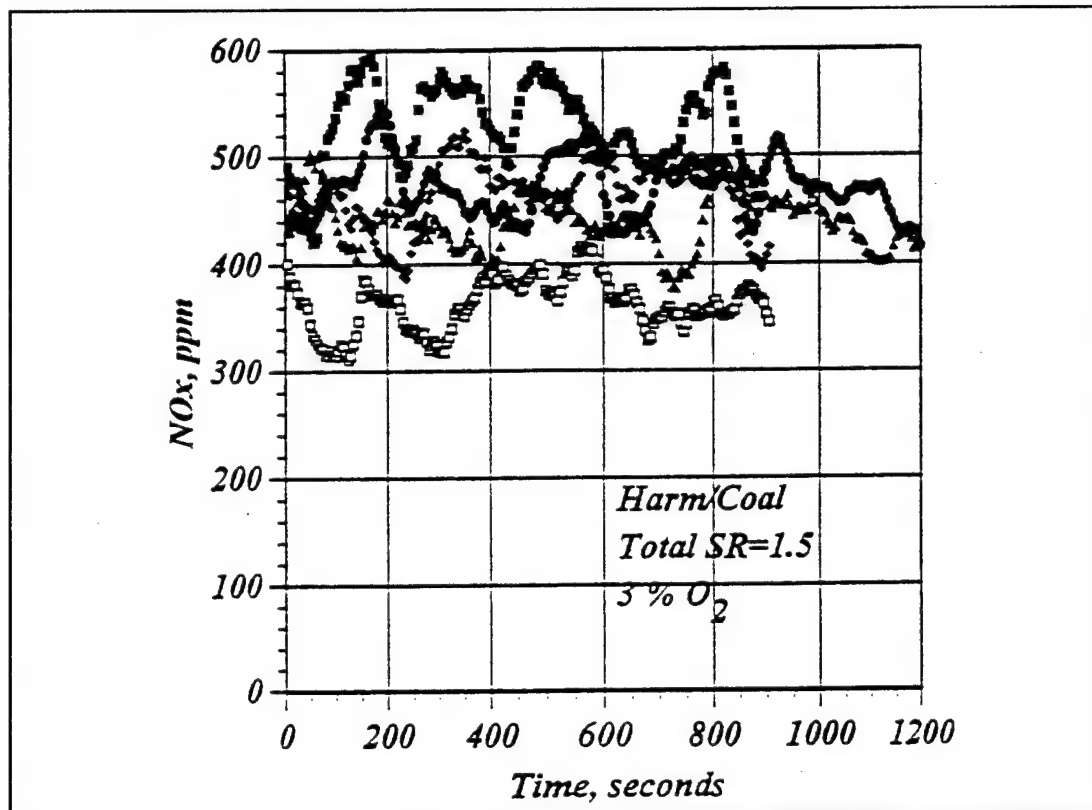


Figure 28. Nitric oxide traces for bed-region stoichiometric ratios for the cofiring of coal and residue in the spreader stoker.

higher than those in Figure 27, but it permits the comparison of the data with that from other facilities. Nitric oxide results are commonly reported after correction to 3 percent O_2 . Finally, the NO , CO_2 , and O_2 concentrations are plotted in Figure 29 on a dry, as-measured basis for a bed region stoichiometric ratio of 0.78.

Visual observations of the residue combustion on the stoker bed suggest that the residue's high moisture content kept it relatively cool. The lumps of residue appeared black against the bed of glowing coal particles for the entire time they remained big enough to see. The lumps of residue gradually shrank until they were lost from view.

Special Concerns Related to the High Chlorine Content of the Residue

Any fuel or waste material with a high chlorine content has the potential of producing chlorinated dioxins and furans (Gullett et al. 1994). The HARM residue is 2.0 percent weight percent chlorine. Dioxins and furans are formed downstream of the main combustion chamber at temperatures in the range of 300 to 400 °C. Because of the high chlorine content of the residue, its use as a fuel increases the potential for the formation of dioxins and furans. For this reason it is recommended

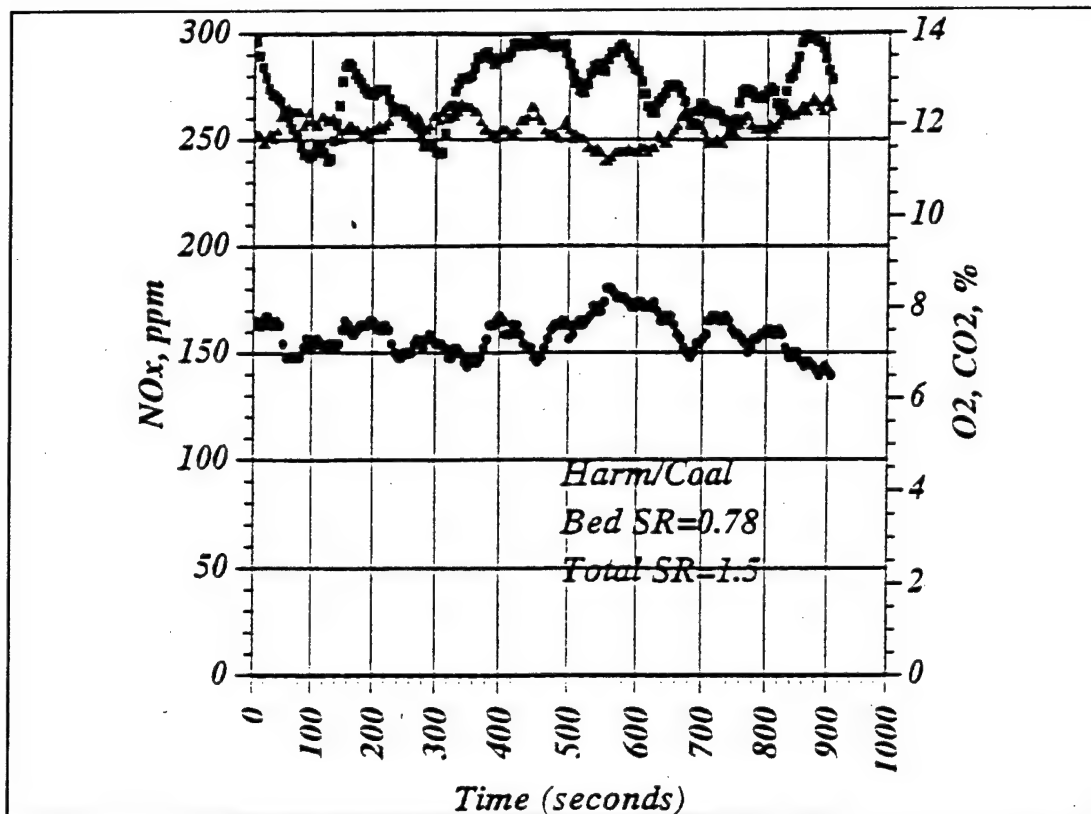


Figure 29. Nitric oxide, oxygen, and carbon dioxide traces for the cofiring of coal and residue in the spreader stoker at a bed region stoichiometric ratio of 0.78.

that the residue be blended with coal or other low-chlorine fuels so the weight fraction of the propellant is kept low.

Conclusions

Based on the pilot-scale rotary kiln and spreader stoker tests described above, it appears that the HARM propellant residue can be safely burned, at the condition examined, as a way of recovering energy from what would otherwise be a waste material. Other conclusions that can be drawn from the experimentation performed for this research include:

- Reducing the moisture content of the residue greatly increases its rate of combustion.
- NO emissions during cofiring the residue and coal can be significantly reduced by staging the spread stoker combustion.
- A 37 percent reduction in NO was achieved by operating the stoker with a stoichiometric ratio of 0.78 in the bed region.
- Further reductions in the exhaust NO could be achieved by using lower bed region stoichiometries.

5 Market Research

Researchers evaluated industries that use solid fuel combustion processes with which a feed source containing AP-depleted binder residue could be integrated. Three basic types of heat generation processes were identified; direct fire drying, steam generation, and direct furnace heat generation. Examples of these types of processes and specific requirements for certain industries are presented in the remainder of this chapter.

Direct Fire Drying

Direct fire drying is used in dehydration processes (salt, cement, raw chemicals, etc.) and in ceramic-lined kiln processes. The major current energy sources for these processes are low sulfur coal and natural gas. Rotary kilns and fluidized beds are used in a majority of the manufacturing facilities. These operations are generally very high volume and are able to pay very low prices for the fuel. Hundreds of thousands of pounds of coal are used at about \$14/ton.

Specific contacts were made with Portland cement processors. These processors are attractive candidates for binder residue processing, as most are equipped to handle coal in a stoker-type arrangement. Residue could therefore be delivered in a large granular form. The companies contacted would like to integrate low-cost residue as a substantial part of their feedstock and would therefore require thousands of pounds of residue on a regular, delivered schedule.

Steam Generation

Steam generation for building heat, process heat, and electricity generation represents a substantial industry. Almost every industrial facility uses steam generation in their processes, and uses these types of fuel sources: coal, diesel, natural gas, wood, etc. The large industrial use processes generally require specific feeding mechanisms, which necessitate specific feedstock configurations.

Discussions were held with Utah Power and Light (UP&L) about integration of binder residue with their electrical power generation plants. Because UP&L use substantial quantities of coal, binder residue could at most represent only a small fraction of their feedstock. It would be necessary, therefore, that the binder residue be completely compatible with the coal slurry feed system used in their boilers. To be compatible would necessitate a complex treatment of the residue to obtain the required pulverized state. The cost of the residue to UP&L would have to be very low, for there would be no other advantage to integrating such a negligible amount of an alternate fuel to the feed source.

Direct Furnace Heat Generation

Foundries and other ore processors use coal or coke to fire open hearth furnaces that directly heat and melt the ore. These industries use large quantities of fuel, which is obtained for a very low price. Researchers contacted a cast iron foundry that has a furnace equipped to handle scrap and low-grade fuels. The binder residue could be integrated very easily into this system as is. This company is interested in high volumes of the residue (thousands of pounds per year), which may be difficult to support. The fuel sources presently used are extremely cheap because most are essentially waste materials.

6 Conclusions and Recommendations

Conclusions

Researchers completed the first phase of identification and evaluation of alternate uses for Class 1.3 reduced smoke propellant binder residue, with the following conclusions:

1. Preliminary data indicate that both the HARM and Maverick propellant binder residues are suitable for use as a low-grade fuel.
2. Because the Sidewinder propellant residue contains approximately 20 percent RDX, additional safety evaluations are necessary to determine if the Sidewinder propellant binder residue could be combusted in bulk quantities.
3. Because all of the binder residues have high moisture contents, additional dewatering would increase their fuel values.
4. Market research has identified three potential combustion reuse options. All of the applications require a very high volume of fuel at a low price.
5. Combustion emissions may be an environmental concern, depending on how the residue is integrated into the system (rates, moisture level, co-fired, etc.)

Recommendations

Additional pilot-scale spreader stoker test are recommended to optimize the reduction of NO emissions during the cofiring of residue and coal. Before full-scale combustion of this material is attempted, it is also recommended that pilot-scale tests be performed to simulate the conditions of the full-scale system. These additional tests could, if desired, include downstream sampling of cooler combustion gases to estimate levels of dioxin and furan emissions at full-scale.

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Abbreviations and Acronyms

ABL	Allegheny Ballistics Laboratory
AEC	Army Environmental Center
AP	ammonium perchlorate
CHN	carbon-hydrogen-nitrogen
DDT	deflagration-to-detonation test
DI	distilled deionized (water)
DSC	differential scanning calorimetry
DST	detonation susceptibility test
GCMS	gas chromatography/mass spectroscopy
HPLC	high performance liquid chromatography
IC	ion chromatography
ICP	inductively coupled plasma
ICP-AES	inductively coupled plasma-atomic emission spectroscopy
MS	mass spectroscopy
RDS	rheometrics dynamic spectroscopy
RDX	cyclotrimethylenetrinitramine
RT	retention time
SBAT	simulated bulk autoignition test
TC	Thiokol Corporation
TCP	tricalcium phosphate
TGA	thermogravimetric analysis

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